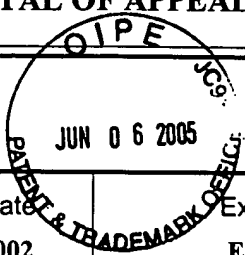


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TRANSMITTAL OF APPEAL BRIEF (Small Entity)

Docket No.  
07820001AA

In Re Application Of: Oyama



Application No.  
10/089,515

Filing Date  
07/03/2002

Examiner  
E. Wood

Customer No.  
30743

Group Art Unit  
1755

Confirmation No.  
7837

Invention: NOVEL TRANSITION METAL PHOSPHIDE CATALYSTS

COMMISSIONER FOR PATENTS:

Transmitted herewith in triplicate is the Appeal Brief in this application, with respect to the Notice of Appeal filed on: April 21, 2005.

☒ Applicant claims small entity status. See 37 CFR 1.27

The fee for filing this Appeal Brief is: \$250.00

☒ A check in the amount of the fee is enclosed.

☐ The Director has already been authorized to charge fees in this application to a Deposit Account.

☒ The Director is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. 50-2041

☐ Payment by credit card. Form PTO-2038 is attached.

**WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.**

Signature

Dated: June 6, 2005

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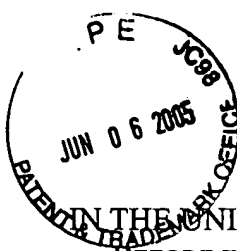
I hereby certify that this correspondence is being deposited with the United States Postal Service with sufficient postage as first class mail in an envelope addressed to "Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450" [37 CFR 1.8(a)] on

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Typed or Printed Name of Person Mailing Correspondence

CC:



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE  
BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES

In re patent application of S. T. Oyama

Group Art Unit 1755

Serial No. 10/089,515

Examiner Elizabeth Wood

Filed July 3, 2002

Confirmation No. 7837

For: ***NOVEL TRANSITION METAL PHOSPHIDE CATALYSTS***

MAIL STOP APPEAL BRIEF

Commissioner for Patents

P.O. Box 1450

Alexandria, Virginia 22313-1450

APPELLANT'S BRIEF UNDER 37 C.F.R. § 41.37

In response to the action of the Primary Examiner in finally rejecting claims 1-11 of this application, a Notice of Appeal was timely filed April 21, 2005. This brief, which is filed herewith in triplicate, is in furtherance of the Notice of Appeal.

This brief contains these items under the following headings and in the order set forth below, as required under 37 C.F.R. § 41.37:

- I. REAL PARTY IN INTEREST
- II. RELATED APPEALS AND INTERFERENCES
- III. STATUS OF CLAIMS
- IV. STATUS OF AMENDMENTS
- V. SUMMARY OF CLAIMED SUBJECT MATTER
- VI. GROUNDS OF REJECTION TO BE REVIEWED ON APPEAL
- VII. ARGUMENTS
  - ☐ ARGUMENT VIIA. REJECTIONS UNDER 35 U.S.C. §112, FIRST PARAGRAPH

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☐ ARGUMENT VIIB. REJECTIONS UNDER 35 U.S.C. §112, SECOND  
PARAGRAPH

☐ ARGUMENT VIIC. REJECTIONS UNDER 35 U.S.C. §102

☒ ARGUMENT VIID. REJECTIONS UNDER 35 U.S.C. §103

☐ ARGUMENT VIIE. REJECTION OTHER THAN 35 U.S.C. §§102, 103  
AND 112

VIII. CLAIMS APPENDIX

IX. EVIDENCE APPENDIX

X. RELATED PROCEEDINGS APPENDIX

## I. REAL PARTY IN INTEREST

The real party in interest in the appeal is:

☐ the party named in the caption of this brief.

☒ the following party:

Oyama Technical Consulting, LLC., of Blacksburg, Virginia

## II. RELATED APPEALS AND INTERFERENCES

With respect to other appeals or interferences that will directly affect, or be directly affected by, or have a bearing on the Board's decision in this appeal:

☒ there are no such appeals or interferences.

☐ these are as follows:

### III. STATUS OF CLAIMS

The status of the claims in this application is as follows:

A. Total number of claims in Application

The claims in the application are: Claims 1, 3-7, 9-13, and 40-43,  
totaling 15 claims

B. Status of all the claims:

1. Claims cancelled: 2, 8, 14-39
2. Claims withdrawn from consideration but not cancelled: None
3. Claims pending: Claims 1, 3-7, 9-13, 40-43
4. Claims allowed: 40-42
5. Claims rejected: Claims 1, 3-7, 9-13, and 43
6. Claims objected to: None

C. Claims on Appeal.

The claims on appeal are: Claims 1, 3-7, 9-13, and 43

#### IV. STATUS OF AMENDMENTS

The status of amendments filed subsequent to the final rejection is as follows:

A response without amendment was filed on March 28, 2005. In the Advisory Action, the Examiner indicated claims 40-42 were allowed, and that the remaining claims were rejected for the reasons of record. Based on this, it is presumed that the response fully addressed the rejection to claim 42 lodged under 35 U.S.C. 112, second paragraph.

## V. SUMMARY OF THE CLAIMED SUBJECT MATTER

The application describes catalysts that are useful for hydrotreating hydrocarbon feedstocks.

Independent claim 1 requires that the catalyst include

“a metal phosphide complex having the formula  $MP_x$ , wherein M is selected from the group consisting of V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W, and wherein x ranges from about 0.1 to about 10”

The metal phosphide complexes meeting this criteria are specifically discussed on page 9, lines 1-3 of the application.

Independent claim 1 requires that the catalyst include a support material as follows

“a high surface area support of at least  $50\text{m}^2/\text{g}$ , wherein the metal phosphide complex is dispersed on the high surface area support, wherein said high surface area support is selected from the group consisting of carbon, silica, titania, thoria, magnesia, zirconia, kaolin, bentonite, kieselguhr, zeolites, and combinations thereof”

The high surface areas supports are specifically described on page 10 of the application at line 1-11.

Examples 2-6 on pages 13-17 of the application describe the formation of various catalysts which fall within the ambit of claim 1.

Independent claim 7 is directed to a mixed metal phosphide catalyst, and requires that the catalyst include:

“a metal phosphide complex having the formula  $A_aB_bP_y$ , wherein A and B are each selected from the group consisting of V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W, wherein the sum of a and b is 1, the ratio of a and b ranges from about 0.01 to about 100, and y ranges from about 0.1 to about 10”

Mixed metal complexes are specifically describe on page 9 of the application at lines 4-14 (lines 12 and 13 giving specific examples).

Independent claim 7, similar to independent claim 1, requires that the metal



phosphide complex be present on a high surface area support as follows:

“a high surface area support of at least 50m<sup>2</sup>/g, wherein the metal phosphide complex is dispersed on the high surface area support, wherein said high surface area support is selected from the group consisting of carbon, silica, titania, thoria, magnesia, zirconia, kaolin, bentonite, kieselguhr, zeolites, and combinations thereof”.

The high surface area supports are specifically described in the application at page 10 at lines 1-11.

Example 7 on page 17 of the application provides a specific example of a mixed metal catalyst that is within the ambit of claim 7.

## VI. GROUNDS OF REJECTION TO BE REVIEWED ON APPEAL

1) Are claims 1, 3-7, 9-13 and 43 obvious over U.S. Patent 4,454,246 to Fung or U.S. Patent 4,359,406 to Fung?

2) Are claims 1, 2 and 4 obvious over Journal of Catalysis (XP009009979) in view of either U.S. Patent 4,454,246 to Fung or U.S. Patent 4,359,406 to Fung?

3) Are claims 1, 3-7, and 9-13 obvious over U.S. Patent 4,367,137 to Antos?

ARGUMENT VIIA. REJECTIONS UNDER 35 U.S.C. §112, FIRST PARAGRAPH

There are no rejections under 35 U.S.C. §112, first paragraph.

ARGUMENT VIIB. REJECTIONS UNDER 35 U.S.C. §112, SECOND PARAGRAPH

There are no rejections under 35 U.S.C. §112, second paragraph. As noted above, it is presumed that the amendment after final rejection filed March 28, 2005 fully addressed the rejection lodged under 35 U.S.C. §112, second paragraph.

ARGUMENT VIIC. REJECTIONS UNDER 35 U.S.C. §102

There are no rejections under 35 U.S.C. §102.

## ARGUMENT VIID. REJECTIONS UNDER 35 U.S.C. §103

The Declaration of Dr. Oyama, attached hereto and filed in the application on November 18, 2004, establishes that the two Fung references and the Antos reference deal with “noble” metal phosphides, not the base metal phosphides contemplated by this invention (see page 3 of Declaration), and that the processes employed by Fung and Antos would not yield metal phosphides as contemplated by the invention (see data on page 5 of the declaration with respect to Fung references; and conclusions (supported by literature references on page 6 of the declaration with respect to Antos).

### Fung Patents

Both Fung patents describe a procedure for the impregnation of a support with soluble metal compounds, a phosphorous source, and the direct reduction of the compounds in hydrogen, without high temperature calcination. Evidence in the case establishes unequivocally that such procedures would not be successful for producing metal phosphides from non-noble metals, as are specified in independent claims 1 and 7 of the application.

Dr. Oyama’s declaration establishes scientifically that **non-noble** metal phosphides cannot be formed by the process of Fung. It does **not** dispute or take issue with the formation of  $PtP_2$  by the direct reduction procedures in Fung. Note particularly pages 4 and 5 of Dr. Oyama’s declaration where it is demonstrated that if you do not first calcine the metal precursors at high temperature to form a phosphate, and then perform reduction on the phosphate (as is disclosed in the present application), metal phosphide catalysts will not be produced (Fung describes direct reduction without prior phosphate formation—this works for Pt phosphides, but not the non-noble metal phosphides contemplated by this invention and which are specifically set forth in independent claims 1 and 7).

As is demonstrated in the table on page 5 of Dr. Oyama’s declaration, if Fe, Co,

and Ni metal precursors are subject to reduction without prior phosphate formation, and under the same temperature conditions as described in the Fung patents a metal, **not a metal phosphide**, is produced. However, when the same metal precursors are calcined to form a phosphate, where the positive metal ion is combined with the negative phosphate species, and then reduced under higher temperatures, **a metal phosphide is produced, not a metal**. As such, the data presented in the declaration of Dr. Oyama, clearly and unequivocally, establishes that the direct reduction of components, as is contemplated in the Fung references, does **not** work for the base metals recited in the claims of the present application. Dr. Oyama's declaration does not attack or dispute Fung's methodology and results with platinum. Rather, it establishes that for non-noble metals, you must first combine the metal and phosphorous in order to make a metal phosphide. Further, as the Examiner should acknowledge, Fung presents no **evidence** whatsoever of the formation of any other metal phosphides other than platinum phosphides. Rather, Fung only references that the possibility of forming other phosphides such as iron, cobalt, and nickel. However, Dr. Oyama's data clearly establish that these phosphides cannot be made by the processes contemplated by Fung. Further, the Examiner should note that claim 1 of U.S. patent 4,454,246 to Fung is limited to a **noble** metal phosphide, most likely because that is all Fung provides an enabling disclosure for.

Finally, the Examiner's reference to the possible use of higher temperatures being contemplated in Fung (e.g., 650°C) is not on point. It should be understood by the Examiner that once reduction of the precursor to a **metal** has occurred, as is demonstrated in the table on page 5 of the declaration, there is **no chance** that a metal phosphide will then be formed from the metal (i.e., the metal precursor has already been reduced to a metal). Hence higher temperatures would have absolutely no effect on the already reduced metal compound. What is important, and is established unequivocally by the declaration is that you must first combine the non-noble metal and the phosphorous, such as by forming a metal phosphate by high temperature calcining. Once the metal and the phosphorous are combined, reduction will result in the formation of metal phosphides of non-noble metals (see the table on page 5 of Dr. Oyama's declaration as well as all of the

test results in the Examples section of the present application at pages 12-21).

Comments in the Advisory Action relative to the Fung Patents

The Examiner states the following:

“Finally, applicant continues to argue that Fung is not operative; the examiner will have no further comment on the Fung disclosures. The references explicitly disclose some of the same metals being claimed herein by applicant used to make phosphides at temperatures up to 650C. The examiner does not have the authroity [sic] to entertain arguments regarding the validity of the disclosures in these U.S. Patents.”

The Examiner’s conclusions about Fung are clearly erroneous, and the Examiner’s refusal to consider uncontroverted data presented in a declaration is in error.

As discussed in detail above, Fung does not show a calcining step. Thus, Fung has a direct reduction with no prior phosphate formation. The table on page 5 of the Oyama declaration demonstrates that, for the metals recited in independent claims 1 and 7, if there is no calcination step performed (i.e., phosphate formation), the metal results from direct reduction, not the metal phosphide. If temperatures of 650C were used, the metal would form, because, as demonstrated from the table on page 5 of the Oyama declaration, direct reduction of non-noble metals results in metal formation, not phosphide formation.

Uncontroverted technical data such as that presented in the Oyama declaration should be accorded proper weight, especially when neither Fung reference presents ANY data concerning phosphide formation with non-noble metals (and, as noted above, U.S. patent 4,454,246 to Fung is limited to a **noble** metal phosphide).

Because neither Fung reference presents a methodology which would result in non-noble methal phosphide formation, as is clearly required in independent claims 1 and 7, neither Fung reference would make claimed invention obvious to one of ordinary skill in the art.



## Antos

Antos describes an acidic catalytic composite composed of a carrier metal supporting a platinum group metal, cobalt, tin, phosphorous and halogen. Antos never states that a phosphide is formed, as is required in the present invention. Rather, Antos, at column 14, states that it is not known what chemistry is formed by his procedures.

As noted above with Fung, direct reduction of a non-noble metal does not result in phosphide formation. Further, evidence of record in the case establishes that Antos does not result in the formation of a metal phosphide. Note particularly page 6 of the Oyama declaration where it is noted that the temperature used by Antos is too low for phosphide formation. The Oyama declaration is supported by evidence in a published article to Wang (on which Dr. Oyama is a joint-author) where, in Figure 4 on page 325 it is demonstrated reduction occurs between 550C and 690C.

Given the data in the Wang article presented in the Oyama declaration, and the stated uncertainty in Antos, the only conclusion one of ordinary skill of art would drawn is that Antos does not form metal phosphides within the ambit of independent claims 1 and 7 of the present application.

## Comments in the Advisory Action on the Antos Patent

The Examiner takes the position that the data in the Wang article and the data and arguments in the Oyama declaration were conflicting. This is simply in error.

First, as the Examiner will recognize, Oyama is a joint author of the Wang article, and is the declarant of the declaration. The data in the Wang article and the data in the Oyama declaration are not in any way in conflict. Furthermore, the data in the Wang article and the data in the application are not in conflict. Note particularly that the results in Wang correspond directly with the results in Example 5 of the application (see page 16 of the application for synthesis of a cobalt phosphide).

Second, at the bottom of page 6 and at the top of page 7 of the Oyama declaration

it is stated “Wang et al., *J. Catalysis* 208:321-332(2002). This document, on which I am noted as a joint-author, shows that with Co/P, major reduction took place at 820K (550°C), but completion required 690°C.” (Emphasis added). With this in mind, the Examiner’s conclusion that “if his own examples require higher temperatures for the completion of formation, this is not evidence of non-obviousness”, is categorically wrong. The evidence establishes major reduction at 550°C , which is higher than Antos 524°C. Major reduction means formation of the phosphide occurs at this temperature. Thus, the Examiner has erroneously made conclusions which incorrectly contradict the evidence presented in the case and in published journal articles. Moreover, as is noted in the response filed March 28, 2005, the Goodenough reference is not in conflict with the claimed invention, the declaration of Oyama, or the Wang references. The reference discloses use of 850°C when forming metal phosphides (see page 1251) (there is no statement that a temperature is required).

With reference to the Oyama declaration, the Wang reference and the Goodenough reference, and the admission in Antos that the chemistry of the product was not known, the one correct conclusion that can be derived is that Antos does not show a metal phosphide. The temperature employed is too low. Given the teachings of Antos, one of ordinary skill in the art would not have been able to produce the claimed non-noble metal phosphides of the present application (see claims 1 and 7).

Combination of Fung patents and Nozaki (*J. Catalysis* (XP009009979))

As noted in detail above, Fung describes a process which does not utilize a calcination step prior to reduction. Fung's process is suitable for making noble metal phosphides, as is supported by the data in the Fung references and as required in the claims of the Fung references.

Nozaki describes catalysts on an alumina support. Neither claim 1 nor claim 7 specify alumina as a possible support for the claimed invention. Furthermore, the declaration of Oyama establishes that the choice of support matters, and that alumina is a relatively poor support for phosphides. See particularly page 7 of the Oyama declaration and the attached Figures 1-4 of the Oyama declaration (all of which are taken from published journal articles authored by Dr. Oyama).

With reference to the declaration of Oyama, it can be seen that there is tangible evidence in the case (data in Figures 1-4 of the declaration) that demonstrate use of alumina as a support necessitates higher temperatures for reduction. This is due to the strong interaction of phosphorus with aluminum to produce aluminum phosphate. In particular, MoP/SiO<sub>2</sub> required only 547°C for phosphide formation, while MoP/Al<sub>2</sub>O<sub>3</sub> required 900°C for phosphide formation. Similarly, Ni<sub>2</sub>P supported on two different zeolites required 590-610°C for phosphide formation, while Ni<sub>2</sub>P on alumina required 1000°C for phosphide formation.

In view of this evidence, the only correct conclusion which can be drawn is that the choice of support matters. Thus, the fact that claims 1 and 7 do not require alumina should not be overlooked or minimized in importance.

Furthermore, if either Fung reference were combined with Nozaki, all that would

be created is a metal on alumina. This is because the Fung methods necessarily result in metal formation, not metal phosphide formation, and because Nozaki teaches the use of an alumina support. Thus, claims 1 and 7 of the present application would not be obvious to one of ordinary skill in the art in view of any combination of Fung and Nozaki.

#### Conclusions

- 1) Claims 1, 3-7, 9-13 and 43 are not obvious over either Fung reference.
- 2) Claims 1, 2 and 4 are not obvious over a combination of either Fung reference and Nozaki.
- 3) Claims 1, 3-7, and 9-13 are not obvious over Antos.

ARGUMENT VIIIE. REJECTION OTHER THAN 35 U.S.C. §§102, 103 AND 112

There are no rejections in the case lodged on grounds other than 35 U.S.C. §§102, 103, and 112.

## VIII. CLAIMS APPENDIX

The text of the claims involved in this Appeal are:

1. A catalyst comprising:

a metal phosphide complex having the formula  $MP_x$ , wherein M is selected from the group consisting of V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W, and wherein x ranges from about 0.1 to about 10; and

a high surface area support of at least  $50\text{m}^2/\text{g}$ , wherein the metal phosphide complex is dispersed on the high surface area support, wherein said high surface area support is selected from the group consisting of carbon, silica, titania, thoria, magnesia, zirconia, kaolin, bentonite, kieselguhr, zeolites, and combinations thereof.

3. The catalyst of claim 1 further comprising a promoter selected from the group consisting of the alkali metals, alkaline earth metals, platinum group metals, rhenium, copper, halides, boron, carbon, nitrogen, aluminum, sulfur, gallium, germanium, arsenic, tin, antimony, bismuth, selenium and tellurium.

4. The catalyst of claim 1 wherein x ranges from about 0.5 to about 3.

5. The catalyst of claim 1 wherein the metal phosphide complex is deposited on the support in the range of about 1 to about 40% by weight complex to support.

6. The catalyst of claim 1 wherein the metal phosphide complex is deposited on the support in the range of about 10 to about 30% by weight complex to support.

7. A metal phosphide catalyst comprising:

a metal phosphide complex having the formula  $A_aB_bP_y$ , wherein A and B are each selected from the group consisting of V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W, wherein the sum of a and b is 1, the ratio of a and b ranges from about 0.01 to about 100, and y ranges from about 0.1 to about 10; and

a high surface area support of at least  $50\text{m}^2/\text{g}$ , wherein the metal phosphide complex is dispersed on the high surface area support, wherein said high surface area support is selected from the group consisting of carbon, silica, titania, thoria, magnesia, zirconia, kaolin, bentonite, kieselguhr, zeolites, and combinations thereof.

9. The catalyst of claim 7 further comprising a promoter selected from the group consisting of the alkali metals, alkaline earth metals, platinum group metals, rhenium, copper, halides, boron, carbon, nitrogen, aluminum, sulfur, gallium, germanium, arsenic, tin, antimony, bismuth, selenium and tellurium.

10. The catalyst of claim 7 wherein the ratio of a to b ranges from about 0.1 to about 10.

11. The catalyst of claim 7 wherein the ratio of a to b ranges from about 0.2 to about 5 and wherein y ranges from about 0.5 to about 3.

12. The catalyst of claim 7 wherein the metal phosphide complex is deposited on the support in the range of about 1 to about 40% by weight complex to support.

13. The catalyst of claim 7 wherein the metal phosphide complex is deposited on the support in the range of about 10 to about 30% by weight complex to support.

43. The catalyst of claim 1, wherein the support has a surface area of at least about 100 m<sup>2</sup>/g by BET method.



## IX. EVIDENCE APPENDIX

A declaration of the inventor was filed under 37 C.F.R. 1.132 on November 18, 2004, and a copy of the declaration is attached hereto.

X. RELATED PROCEEDINGS APPENDIX

No decisions have been rendered in any court or by the Board in a related appeal or interference.

Respectfully submitted,

A handwritten signature in black ink, appearing to read 'Michael E. Whitham', written in a cursive style.

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# Synthesis, Characterization, and Hydrotreating Activity of Several Iron Group Transition Metal Phosphides

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Received September 20, 2001; revised March 9, 2002; accepted March 9, 2002

A series of iron, cobalt, and nickel metal phosphides of chemical formula  $\text{Fe}_2\text{P}$ ,  $\text{CoP}$ , and  $\text{Ni}_2\text{P}$  with specific surface areas of around  $3 \text{ m}^2 \text{ g}^{-1}$  were synthesized by means of temperature-programmed reduction (TPR) of the corresponding phosphates. These phosphides were also successfully prepared in dispersed form on a silica support ( $90 \text{ m}^2 \text{ g}^{-1}$ ) for use as catalysts. The phase purity of these materials was established by X-ray diffraction (XRD), and surface properties were determined by  $\text{N}_2$  BET specific surface area ( $S_g$ ) measurements and CO uptake determinations. The activity of the silica-supported catalysts in hydrodenitrogenation (HDN) and hydrodesulfurization (HDS) was evaluated in a three-phase trickle-bed reactor using a model liquid feed containing 2000 ppm nitrogen as quinoline, 3000 ppm sulfur as dibenzothiophene, 500 ppm oxygen as benzofuran, 20 wt% aromatics as tetralin, and balance aliphatics as tetradecane. The reactivity study showed that the HDS activity sequence for the three samples was  $\text{Ni}_2\text{P}/\text{SiO}_2 > \text{CoP}/\text{SiO}_2 > \text{Fe}_2\text{P}/\text{SiO}_2$ , while the HDN activity followed the sequence  $\text{CoP}/\text{SiO}_2 > \text{Ni}_2\text{P}/\text{SiO}_2 > \text{Fe}_2\text{P}/\text{SiO}_2$ . Compared with a commercial  $\text{Ni-Mo-S}/\gamma\text{-Al}_2\text{O}_3$  catalyst,  $\text{Ni}_2\text{P}/\text{SiO}_2$  had a higher HDS activity (90 vs 76%), but a lower HDN activity (14 vs 38%), based on equal sites loaded in the reactor. The sites were determined by CO chemisorption for the phosphide and low-temperature  $\text{O}_2$  chemisorption for the sulfide. XRD and X-ray photoelectron spectroscopy characterizations of the spent catalysts indicated that the  $\text{Ni}_2\text{P}/\text{SiO}_2$  catalyst was tolerant of sulfur. © 2002 Elsevier Science (USA)

**Key Words:** hydrodesulfurization; hydrodenitrogenation; transition metal phosphides;  $\text{Fe}_2\text{P}$ ;  $\text{CoP}$ ;  $\text{Ni}_2\text{P}$ .

## INTRODUCTION

Demands for a cleaner environment have led to a global tightening in the allowed sulfur content in fuels and increased restrictions on the release of nitrogen oxides. For example, in the case of sulfur the U.S. Environmental Protection Agency (EPA) has issued regulations that would lower its allowed content in diesel fuel from the current 500

to 15 ppmw in 2006, and in gasoline from 300 to 30 ppmw by 2004 (1, 2). For this reason there are considerable efforts being expended to develop new technologies for the production of clean fuels, like adsorption, extraction, oxidation, alkylation, and bioprocessing (3). Currently, however, hydroprocessing appears to be the technologically preferred solution (3). Hydroprocessing refers to a variety of catalytic hydrogenation processes that saturate heteroatomic rings and remove S, N, O, and metals from different petroleum streams in a refinery (4). Because of the tighter environmental regulations new types of catalysts, which are economic, have long life, and possess high activity, are highly desired. In this work we present results on a new type of hydroprocessing catalyst: transition metal phosphides.

Transition metal phosphides have attracted considerable interest for some time because these materials are technologically important as semiconductors, luminescent devices, and electronic components (5). A brief thermodynamic analysis of the potential stability in  $\text{H}_2\text{S}$  was carried out early in 1975 (6), and it was revealed that this group of materials is potentially stable and sulfur resistant. However, the transition metal phosphides as a class of materials have received little attention in the field of catalysis. This is probably because the development of synthetic methods of producing materials with high surface areas was not achieved.

The combination of the iron group metals Co and Ni with Mo and W in commercial hydroprocessing catalysts (7–9) and the use of phosphorus as a promoter (10–12) is well-known. Many workers have studied the effect of phosphorus in sulfide catalysts (13–16), and the topic has been reviewed by Iwamoto and Grimblot (17). It was concluded that in these materials, the phosphorus was found as a phosphate and primarily modified the properties of the support, and only indirectly the active phase. For example, phosphorus altered the acid–base character of alumina and improved dispersion of molybdenum on the support. It also enhanced the solubility of the precursor metals in the preparation stages and allowed the synthesis of high-loading catalysts (18). The effect of phosphorus strongly depended on its content, with an effect that was usually negative at high

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loadings. Phosphorus showed no effect or a small positive effect on the hydrodesulfurization (HDS) of thiophene, and a positive effect on the hydrodenitrogenation (HDN) of quinoline (19), pyridine (20), and piperidine (11). Notwithstanding the considerable studies on promoter effects, until recently phosphorus compounds in the form of phosphides had not been examined in the hydroprocessing field. The first report of the use of the iron group metal phosphides as hydrodenitrogenation catalysts was by Robinson *et al.* (21), who prepared  $\text{Co}_2\text{P}$  and  $\text{Ni}_2\text{P}$  on silica, alumina, and carbon. They reported that carbon and silica were the best supports and that  $\text{Ni}_2\text{P}$ , in particular, was very effective in HDN. These studies were carried out at high conversion, and an assessment of the intrinsic activity is not possible. The first studies on Mo and W phosphides were carried out by Li *et al.* (22), Oyama *et al.* (23), and Clark *et al.* (24), who reported good activity for HDS and HDN. Studies in the Prins group (25) confirmed the activity in HDN, and in a recent comparison of  $\text{Co}_2\text{P}$ ,  $\text{Ni}_2\text{P}$ ,  $\text{MoP}$ ,  $\text{CoMoP}$ , and  $\text{NiMoP}$  (26) it was concluded that the areal activity of  $\text{MoP}$  was the highest. Earlier, the olefin hydrogenation activity of  $\text{Ni}_2\text{P}$  supported on alumina and other phosphides was explored by Nozaki and coworkers (27–29). It was found that the hydrogenation activity for butadiene drastically decreased, in the order  $\text{Ni}_2\text{P} > \text{Co}_2\text{P} > \text{FeP}$ . They also reported that a trace of oxygen could increase the activity of  $\text{Ni}_2\text{P}$  while lowering the activity of Ni for the butadiene hydrogenation reaction. Nickel–phosphorus alloys have been reported also in amorphous form and their activities for hydrogenation have also been studied (30, 31). The amorphous alloy was prepared by an electroless plating technique from mixtures of sodium citrate, nickel sulfate, sodium hypophosphite, sodium acetate, and a silica gel support, or by the chemical reduction of nickel acetate and sodium phosphate with sodium borohydride. The supported material was subjected to various treatments, including oxidation at 403 K and reduction in  $\text{H}_2$  at 553 K. The catalyst was found to be active for the hydrogenation of nitrobenzene (32) and benzaldehyde (33), with a turnover rate similar to that of Ni ( $1 \times 10^{-3} \text{ s}^{-1}$ ). In summary, although there are some reports concerning the catalytic behavior of these phosphides, few studies have concentrated on the subject of hydrodesulfurization and hydrodenitrogenation for application in petroleum refining.

The present work presents an in-depth study of the preparation of transition metal phosphides of the iron group (Fe, Co, Ni) and their evaluation in the hydroprocessing of a model feed mixture. Initially unsupported bulk materials were prepared to provide a reference for the synthesis of supported materials. Several metal-to-phosphorus (M/P) ratios were explored to ascertain which stable phases could be prepared and to determine the conditions for temperature-programmed reduction. Subsequently, the preparation was extended to the supported system to obtain materials of high surface area suitable for

catalytic testing. Silica was chosen as the carrier to minimize support effects and make possible the elucidation of the intrinsic catalytic activity of the phosphides.

## EXPERIMENTAL

### Materials

The support used in this study was a fumed silica (Cabosil, L90). The precursors for iron, cobalt, and nickel were  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Aldrich, 99.99%),  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Aldrich, 99.99%), and  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Aesar, 99%), respectively, while the precursor for P was ammonium orthophosphate  $(\text{NH}_4)_2\text{HPO}_4$  (Aldrich, 99%). The chemicals utilized in the reactivity study were dibenzothiophene (Aldrich, 99.5%), quinoline (Aldrich, 99.9%), benzofuran (Aldrich, 99.9%), tetralin (Aldrich, 99.5%), and tetradecane (Jansen Chimica, 99%). The gases employed were He (Airco, Grade 5), CO (Linde Research Grade, 99.97%), 0.5%  $\text{O}_2/\text{He}$  (Airco, UHP Grade),  $\text{H}_2$  (Airco, Grade 5),  $\text{N}_2$  (Airco, 99.99%), and 30%  $\text{N}_2/\text{He}$  (Airco, UHP Grade).

### Synthesis

Unsupported bulk transition metal phosphides were prepared in two steps. In the first step, phosphate precursors were synthesized by reacting metal nitrates with ammonium phosphate, and in the second step, these phosphates were reduced to phosphides by the method of temperature-programmed reduction. Because the procedures for preparing unsupported bulk iron, cobalt, and nickel phosphates were similar, the preparation of iron phosphate ( $\text{FePO}_4$ ) is used here to illustrate the process. First, 4.9 g (37.13 mmol) of ammonium phosphate  $(\text{NH}_4)_2\text{HPO}_4$  was dissolved in 300  $\text{cm}^3$  of distilled water to form a transparent colorless solution, and 15 g (37.13 mmol) of iron nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) was then added. The clear solution immediately turned into a light color mixture with some precipitate, but stirring resulted in the formation of a transparent solution. In the case of nickel and cobalt, several drops of nitric acid were needed to give rise to a homogenous solution. The water was then vaporized from the solution on a hot plate and the resulting paste was dried at 393 K for 3 h and calcined at 773 K for 6 h in an oven. The amount collected (with some minor losses) was 5.54 g, which corresponds to 36 mmol of iron phosphate of formula  $\text{FePO}_4 \cdot \text{H}_2\text{O}$ . The phosphate was then ground with a mortar and pestle and sieved to 16/20 mesh (0.65- to 1.2-mm-diameter particles). In the second step of preparation, temperature-programmed reduction (TPR) was utilized to convert the phosphate into phosphide. The reduction was carried out in a U-shaped quartz reactor placed in a furnace controlled by a temperature programmer (Omega Model CN 2000). The temperature was raised at  $\beta = 0.0167 \text{ K s}^{-1}$  ( $1 \text{ K min}^{-1}$ ) and was monitored by a local chromel–alumel

TABLE 1

## Quantities Used in the Preparation of Supported Samples

Sample	Silica (g)	Materials used		Catalyst properties	
		Metal nitrate (mol)	(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> (mol)	Phosphide loading (wt% M <sub>r</sub> P)	Metal loading (mol% M)
Fe <sub>2</sub> P/SiO <sub>2</sub>	20	0.0462	0.0231	14	11
CoP/SiO <sub>2</sub>	20	0.0231	0.0231	9.4	6.2
Ni <sub>2</sub> P/SiO <sub>2</sub>	20	0.0231	0.0231	9.4	6.1

thermocouple placed in a thermowell near the center of the reactor bed. The H<sub>2</sub> flow rate was set at 1000  $\mu\text{mol s}^{-1}$  (1500  $\text{cm}^3 \text{min}^{-1}$ ) per g of sample. A portion of the exit gas flow was sampled through a leak valve into a mass spectrometer (Ametek/Dycor Model MA 100) and the masses 2(H<sub>2</sub>), 4(He), 18(H<sub>2</sub>O), 28(N<sub>2</sub>), 32(O<sub>2</sub>), 34(PH<sub>3</sub>), 15(NH), 44(CO<sub>2</sub>), 31(P), and 62(P<sub>2</sub>) were monitored during the experiment, and these were recorded together with the temperature by an online computer. At the end of the temperature program, the sample was cooled in helium to room temperature and was passivated in a 0.5% O<sub>2</sub>/He flow for 2 h.

Phosphide samples supported on a silica support were prepared by modifying the two-step procedure used in the synthesis of the unsupported samples. Aqueous phosphate solutions were obtained as before and were used to impregnate silica by the incipient wetness impregnation method. The quantities used for the three supported samples are listed in Table 1. Prior to use, the silica was dried at 393 K for 3 h and calcined at 773 K for 6 h and was found to have an incipient wetness point of 2.2  $\text{cm}^3 \text{g}^{-1}$ . After impregnation, the powders were dried at 393 K for 3 h and calcined at 773 K for 6 h. The calcined samples were ground with a mortar and pestle, pelletized with a press (Carver, Model C), and sieved to 16/20 mesh size. The TPR process was similar to that used for the bulk samples using the same heating rate,  $\beta = 0.0167 \text{ K s}^{-1}$  (1  $\text{K min}^{-1}$ ).

### Characterization

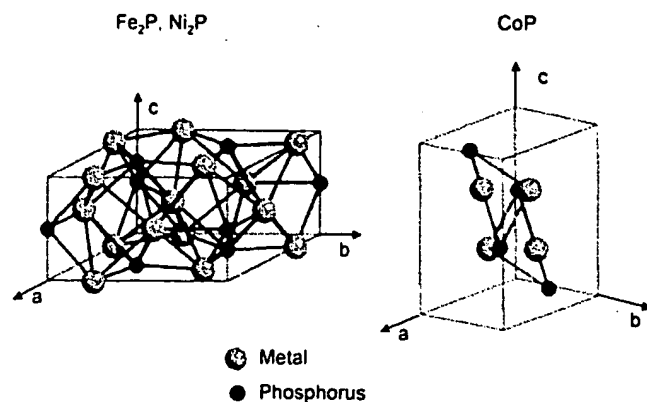
The synthesized materials were characterized by CO chemisorption, N<sub>2</sub> physisorption, and X-ray diffraction (XRD) measurements. Irreversible CO uptake measurements were used to titrate the surface metal atoms and to provide an estimate of the number of active sites on the catalysts. Uptakes were obtained after passivated samples were rereduced and are denoted *ex situ* in this paper. Usually, 0.2 g of sample was loaded into a quartz reactor and treated in H<sub>2</sub> at 723 K for 2 h. After cooling to room temperature in He, pulses of CO in a He carrier flowing at 27  $\mu\text{mol s}^{-1}$  (40  $\text{cm}^3 \text{NTP min}^{-1}$ ) were injected through a sampling valve and the 28 (CO) signal was monitored with a mass spectrometer. Uptakes of CO were also measured

for the spent samples. The procedures were the same as those used for the fresh samples. Prior to the measurement, the spent samples removed from the hydrotreating reactors were washed in hexane and dried.

BET surface area measurements were carried out right after the CO uptake determinations, using a similar technique. Adsorption at liquid nitrogen temperature was performed using a 30% N<sub>2</sub>/He stream, and the desorption area obtained after rapid heating was compared to the area of a calibrated volume (35.4  $\mu\text{mol}$ ). The surface area was calculated from the one-point BET equation, which is reasonable for nonmicroporous materials such as those used here. X-ray diffraction (XRD) patterns of the samples were determined with a Scintag XDS-2000 powder diffractometer operated at 45 kV and 40 mA, using Cu K $\alpha$  monochromatized radiation ( $\lambda = 0.154178 \text{ nm}$ ). The crystallite size of the supported sample was calculated using the Scherrer equation,  $D_c = K\lambda/\beta \cos(\theta)$ , where  $K$  is a constant taken as 0.9,  $\lambda$  is the wavelength of the X-ray radiation,  $\beta$  is the width of the peak at half-maximum, corrected for instrumental broadening (0.1°), and  $2\theta$  is the Bragg angle (34–36). The near-surface composition of the nickel samples was obtained by X-ray photoelectron spectroscopy (XPS) (Perkin-Elmer, Model 5300 with a Mg source) operated at 15 kV and 30 mA. The 285.0-eV binding energy peak of adventitious carbon was used as reference. In the case of the spent catalysts, samples were removed from the reactor, washed in hexane, heated in H<sub>2</sub> to 673 K, and then passivated. Since the samples were exposed to the atmosphere and not sputtered, contamination by carbon from the atmosphere was present.

### Reactivity Studies

Hydrotreating activities of the samples were obtained in a three-phase trickle-bed reactor for hydrodenitrogenation (HDN) and hydrosulfurization (HDS) with a model petroleum liquid containing 2000 ppm nitrogen (quinoline), 3000 ppm sulfur (dibenzothiophene), 500 ppm oxygen (benzofuran), 20 wt% aromatics (tetralin), and balance aliphatics (tetradecane). The operating conditions were close to industrial conditions, 3.1 MPa and 643 K, with a liquid flow rate of 5  $\text{cm}^3/\text{h}$  and a hydrogen flow rate of 100  $\mu\text{mol s}^{-1}$  (150  $\text{cm}^3 \text{min}^{-1}$ ) corresponding to a gas-liquid ratio of 9800 SCF H<sub>2</sub>/barrel. The detailed description of the testing system is reported elsewhere (37). Quantities of catalysts loaded in the reactor correspond to the same amount of *ex situ* CO uptake (35  $\mu\text{mol}$ ). Prior to reactivity measurements, the catalyst samples were pretreated in exactly the same manner as before the *ex situ* CO uptake determinations. Hydrotreating samples were collected every 2 or 3 h in sealed septum vials and were analyzed off-line with a gas chromatograph (Hewlett Packard, 5890A) equipped with a 0.32 mm i.d.  $\times$  50 m fused silica capillary column (CPSIL-5CB, Chrompack, Inc.) and a flame ionization detector.

FIG. 1. Crystal structures of  $\text{Fe}_2\text{P}$ ,  $\text{CoP}$ , and  $\text{Ni}_2\text{P}$ .

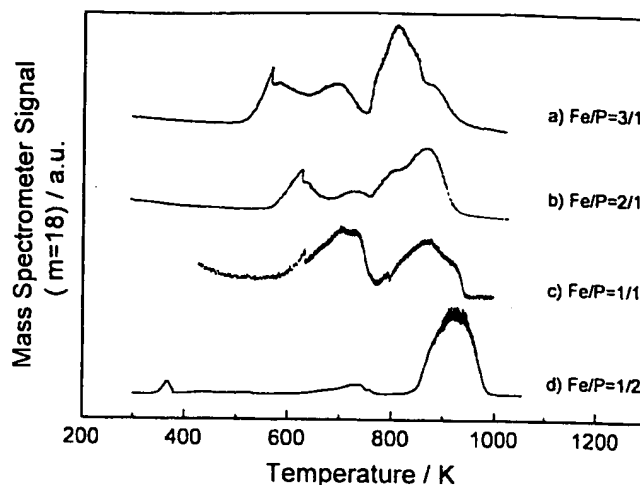
## RESULTS AND DISCUSSION

### Properties and Preparation of Bulk Phosphides

The crystal structures of the Fe, Co, and Ni phosphides are shown in Fig. 1 and their lattice parameters are summarized in Table 2. Both  $\text{Fe}_2\text{P}$  (38) and  $\text{Ni}_2\text{P}$  (39) adopt the same hexagonal structure (space group:  $P_{62m}$ ), while  $\text{CoP}$  (40) takes on an orthorhombic structure (space group:  $P_{nma}$ ). The crystal structures (Fig. 1) and lattice parameters can be used to calculate the bulk density ( $\rho$ ) and the surface metal atom density ( $\bar{n}$ ) of the solids (Table 2). For the  $\text{Fe}_2\text{P}$  and  $\text{Ni}_2\text{P}$  samples there are two, three, and two atoms on the  $ac$ ,  $ab$ , and  $bc$  unit cell faces, respectively. For  $\text{CoP}$ , every unit cell face has two atoms.

The investigation of the phosphide materials in this study was begun by a study of the synthesis of bulk materials of various metal-to-phosphorus ratios (M/P) by the temperature-programmed method. This was carried out to prepare suitable references for the supported materials, and to evaluate the conditions of preparation needed when a support was employed.

The synthesis of the bulk phosphides involved two stages, preparation of phosphate precursors and reduction of the precursors in a temperature-programmed manner. The results for iron are discussed first. The precursors prepared in the first stage had different Fe/P ratios, set at the time of preparation by adjusting the mole ratio of the constituents. The precursors were formed by the thermal decomposition

FIG. 2. Temperature-programmed reduction of bulk iron phosphates at  $\beta = 1 \text{ K/min}$  ( $0.01667 \text{ K s}^{-1}$ ) (Fe-to-P ratios used in the preparation are indicated).

of mixtures of the metal nitrate and ammonium phosphate in air. Because the nitrate and ammonium ions are unstable at high temperature, it was expected that the mixture would decompose to a metal phosphate or metal oxide-phosphate. At high metal ratios some metal oxide was also likely. X-ray diffraction patterns of the precursors showed that they were amorphous.

Temperature-programmed reduction (TPR) of the precursors was carried out in the second stage (Fig. 2). Only the results for mass 18( $\text{H}_2\text{O}$ ) are shown, as the other monitored masses were featureless or provided little additional information. The TPR traces show two systematic trends for the samples with different Fe/P ratios. First, for higher Fe contents (Figs. 2a–2c), the TPR traces show more peaks and a more complicated overall reduction pattern. Second, for higher Fe contents, all the reduction peaks including the initial and final features are shifted to lower temperatures. These trends are reasonable. For higher Fe contents, the precursor is probably a mixture of iron oxide, iron phosphate, and possibly other components, and their separate reduction results in different peaks. Also for these higher Fe contents, the proportion of iron oxide should increase, and since this oxide is easily reducible, its TPR peaks appear at lower temperatures. In fact, it is likely that some metallic

TABLE 2

Surface Metal Density and Bulk Density of  $\text{Fe}_2\text{P}$ ,  $\text{CoP}$ , and  $\text{Ni}_2\text{P}$ 

Sample	Lattice parameter (nm)			Surface metal density ( $10^{15} \text{ atoms cm}^{-2}$ )				Compound density ( $\rho$ ) ( $\text{g cm}^{-3}$ )
	$a$	$b$	$c$	$ab$ plane	$bc$ plane	$ac$ plane	Average ( $\bar{n}$ )	
$\text{Fe}_2\text{P}$	0.5867	0.5867	0.3458	1.01	0.986	0.986	0.994	6.67
$\text{CoP}$	0.5077	0.3281	0.5587	1.20	1.09	0.706	0.999	6.20
$\text{Ni}_2\text{P}$	0.5859	0.5859	0.3382	1.01	1.01	1.01	1.01	7.09

Fe is formed and that it assists in the reduction of the other components. For low Fe contents (Fig. 2d), there is no iron oxide and reaction occurs at the intrinsic reduction temperature of the main phosphate phase ( $\sim 920$  K). Because this temperature is high, even if a mixture of components other than phosphates existed, individual reduction steps cannot be resolved and the whole process appears to occur in one stage.

Analysis of the products of TPR was carried out by XRD (Fig. 3). The diffraction patterns all show a high background because of fluorescence by the iron. However, the presence of distinct iron phosphides can be seen easily. For the samples with Fe/P ratios of 3/1 and 2/1, the XRD results show the expected phases of  $\text{Fe}_3\text{P}$  (Fig. 2a) and  $\text{Fe}_2\text{P}$  (Fig. 3b). Comparison is made with standards from the powder diffraction file (PDF) (41), as indicated in the figure. For the sample with Fe/P ratio of 1/1, the obtained phase was still  $\text{Fe}_2\text{P}$  (Fig. 3c), and there was a deficiency in phosphorus. Similarly, for the sample with an Fe/P ratio of 1/2, the observed phase was  $\text{FeP}$ . Thus, although the preparations were carried out with stoichiometric quantities of metal and phosphorus, the final products tended to be metal-rich.

There are probably several processes which contributed to the loss of phosphorus in these samples. Some of the loss may have occurred during the TPR process, as traces of  $\text{PH}_3$  were detected in the mass spectrometer signal and some volatile products were observed to condense at the exit of the reactor. Some of the loss probably also occurred in the calcination step at 773 K to form the phosphate precursor. A small amount of a white solid was found to have sublimed onto the lid of the ceramic calcination vessel. This was likely to be  $\text{P}_2\text{O}_5$ , with a melting point of 563 K and a sublimation temperature of 787 K. The loss of P was observed in all

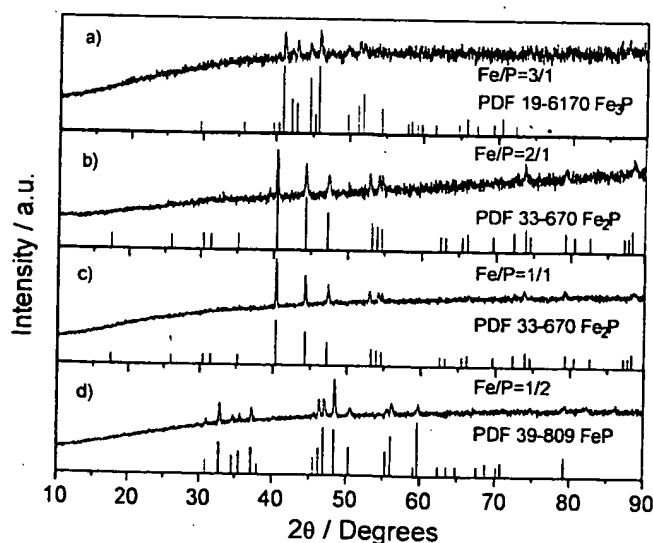


FIG. 3. X-ray diffraction patterns of iron phosphides (PDF file references are also included).

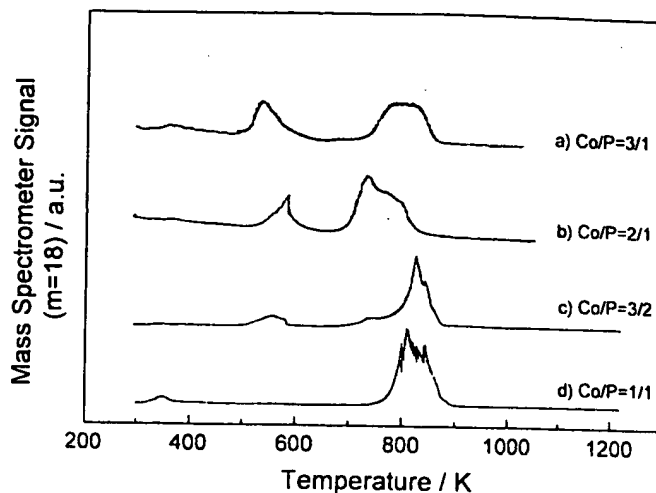


FIG. 4. Temperature-programmed reduction of bulk cobalt phosphates at  $\beta = 1$  K/min ( $0.01667$  K  $\text{s}^{-1}$ ) (Co-to-P ratios used in the preparation are indicated).

samples with high P levels. There is also a possibility that some extra phosphorus in amorphous form remained mixed in the samples, and that the observed phases were simply the stable ones under the preparation conditions.

The trends in the TPR results for the cobalt samples (Fig. 4) are similar to those of the iron samples. The reaction traces consist of two main features, a low-temperature peak and a more complicated high-temperature signal. (The sample with Co/P = 1/1 has a small feature at  $\sim 350$  K, probably due to dehydration). The low-temperature peak appears between 500 and 600 K and is more intense for higher Co contents (Figs. 4a–4c). It also shifts to lower temperature with increasing Co content. This behavior is consistent with the reduction of a cobalt oxide species. The higher temperature signal appears between 700 and 900 K and probably corresponds to the reduction of cobalt phosphate, which is expected to be more difficult to reduce. It is the main feature for the Co/P = 1/1 sample (Fig. 4d). The XRD patterns of the reduced cobalt samples (Fig. 5) show that  $\text{Co}_2\text{P}$  was obtained from the samples with Co/P ratios of 3/1, 2/1, and 3/2 (Figs. 5a–5c), and CoP was obtained as expected from the sample with a Co/P ratio of 1/1 (Fig. 5d). It appears that  $\text{Co}_2\text{P}$  is a particularly stable phase at these conditions.

The same trends in the TPR traces were also observed with the nickel samples (Fig. 6). The reduction features were a composite of different peaks, occurring at a low-temperature range of 500–700 K, and at a high-temperature range of 700–850 K. These various features are attributed again to the reduction of different compounds, likely nickel oxides and nickel oxide phosphate at the low temperatures and nickel phosphate at the high temperatures. As expected,  $\text{Ni}_3\text{P}$  was observed in the sample with a Ni/P ratio of 3/1 (Fig. 7a). But for the Ni/P ratios of 2/1, 3/2, and 1/1 (Figs. 7b–7d), the phase obtained was  $\text{Ni}_2\text{P}$ . Probably, this is

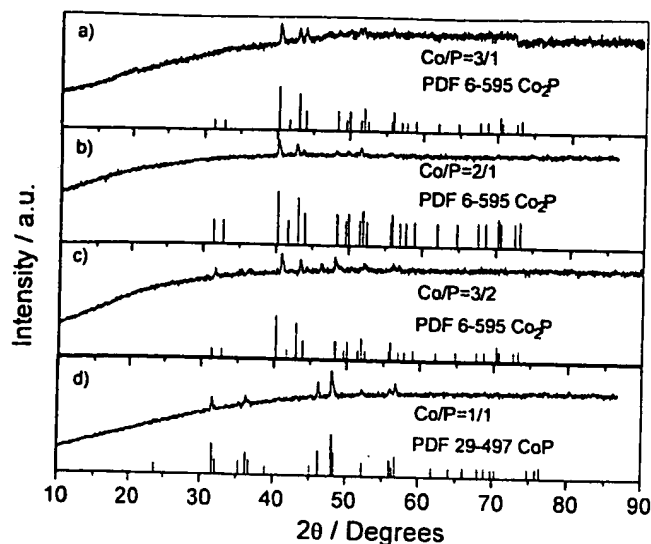


FIG. 5. X-ray diffraction patterns of reduced cobalt phosphates (PDF file references are also included).

the stable phase at the conditions of the preparation, since not all the phosphorus in the precursor phosphate mixtures is likely to have sublimed. Different from the other samples, the TPR trace of the sample with the Ni/P ratio of 1/1 did show some P and PH<sub>3</sub> during the reduction process. This accounts for the loss of P in this sample.

To summarize these TPR and XRD results, the reduction of phosphate precursors occurs readily in the Fe, Co, and Ni systems, with maximum temperatures of about 900 K. A number of bulk phosphide compounds can be produced, depending on the stoichiometric proportions of M/P used, but the Fe<sub>2</sub>P, CoP, and Ni<sub>2</sub>P products are the preferred phases under the experimental conditions used in this study.

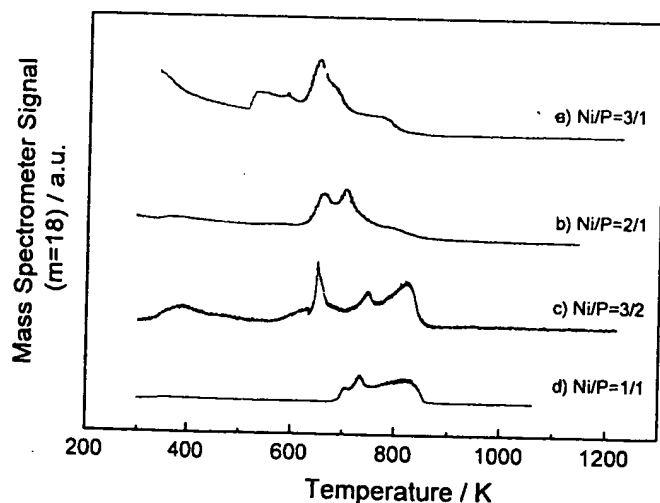


FIG. 6. Temperature-programmed reduction of bulk nickel phosphates at  $\beta = 1$  K/min ( $0.01667$  K s<sup>-1</sup>) (Ni-to-P ratios used in the preparation are indicated).

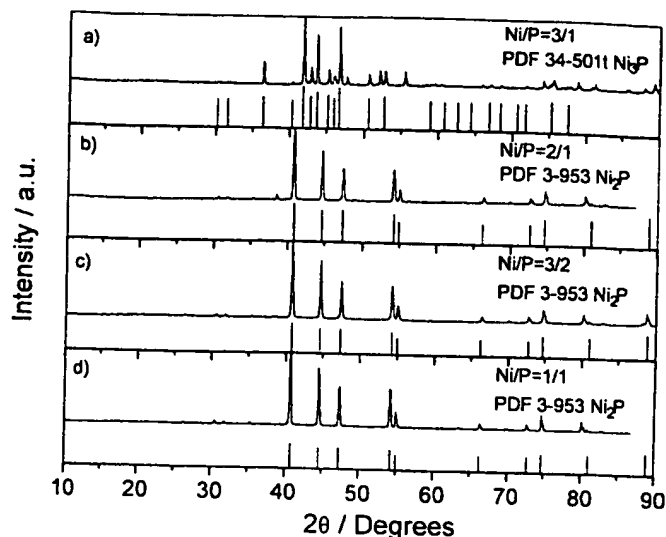


FIG. 7. X-ray diffraction patterns of reduced nickel phosphates (PDF file references are also included).

### Properties and Preparation of Supported Phosphides

In order to study the catalytic properties of the Fe, Co, and Ni samples high-surface-area materials were desired, and therefore, the phosphides were prepared in supported form using silica as the carrier. The preparation involved the same steps used in the synthesis of the bulk compounds. First, phosphates were prepared on the support and then were reduced by TPR. The final temperatures for preparing hydrotreating catalysts were determined by noting the point where the intensity of the water signal returned to baseline in preliminary TPR test measurements on small samples. The final temperature for supported iron, cobalt, and nickel samples were 1000, 900, and 850 K, respectively (Fig. 8). Silica was selected as the carrier because in dehydrated form it has few acid and base sites and is likely to

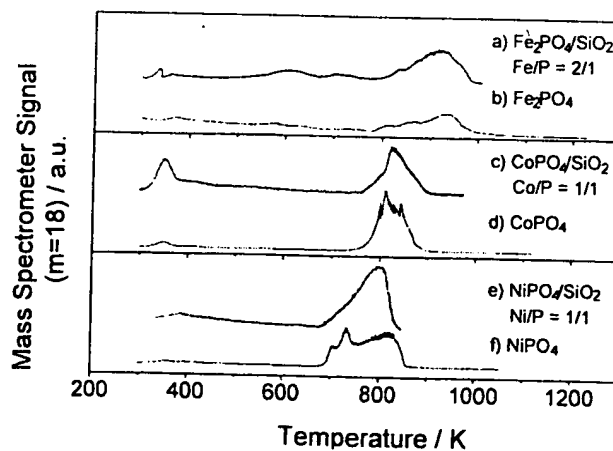


FIG. 8. TPR comparison of supported and unsupported catalysts at  $\beta = 1$  K/min ( $0.01667$  K s<sup>-1</sup>).



TABLE 3

## Characterization Results of Samples

Samples	BET surface area ( $S_g/m^2 g^{-1}$ )	CO uptake ( $\mu mol g^{-1}$ )	$D_p$ (nm)	$D_c$ (nm)	Metal site concentration ( $\mu mol g^{-1}$ )
Fe <sub>2</sub> P	2.7	3	330	38	45
Fresh Fe <sub>2</sub> P/silica	97	16		23	90
Spent Fe <sub>2</sub> P/silica	83	0		23	90
CoP	3.1	3	310	40	51
Fresh CoP/silica	87	16		21	72
Spent CoP/silica	90	4		21	72
Ni <sub>2</sub> P	3.3	4	260	36	55
Fresh Ni <sub>2</sub> P/silica	98	15		20	67
Spent Ni <sub>2</sub> P/silica	100	13		20	67

offer minimal support interaction to affect the properties of the phosphides. Thus, the intrinsic activity of the phosphides could be determined.

Comparison of the TPR results obtained for the bulk samples and the corresponding supported samples (Fig. 8) provides strong evidence that the transformation of the phosphates to phosphides proceeded in the same manner for both bulk and supported samples. Aside from a slightly more pronounced low-temperature dehydration feature for the supported samples, the TPR traces for the samples of iron and cobalt were very similar to those of the unsupported forms. The reduction trace of the supported nickel sample was somewhat simpler than that of the bulk sample, but occurred at essentially the same temperature range.

The characterization results for the bulk and supported samples are reported in Table 3. The specific surface areas ( $S_g$ ) of the bulk materials were low, approximately  $3 m^2 g^{-1}$ , while those of the supported materials were close to that of the support ( $90 m^2 g^{-1}$ ). The experimental CO uptakes of the samples are reported in the third column of Table 3. They were low for the bulk materials but increased for the supported samples.

The particle diameter of the bulk materials was calculated by the equation  $D_p = 6/\rho S_g$  using their surface area and the bulk density (Table 2). The particle sizes for the bulk Fe<sub>2</sub>P, CoP, and Ni<sub>2</sub>P samples were similar, about 260–330 nm (Table 3). The crystallite sizes ( $D_c$ ) were obtained from the Scherrer equation presented in the experimental section. The crystallite sizes for the bulk phosphides were again similar, about 36–40 nm. For all the bulk samples,  $D_p > D_c$ , and this could be due to strain and disorder in the crystallites or crystallite agglomeration. The latter is probably the larger contributor, as no support was used to stabilize the samples.

The last column in Table 3 reports the theoretical metal site concentration assuming that the samples were composed of uniform spherical particles. It was calculated from

the equation

$$\text{Metal site concentration} = S_g \cdot \bar{n} \cdot f,$$

where  $S_g$  is specific surface area,  $\bar{n}$  is the surface metal atom density, and  $f$  is the fractional weight loading (e.g., grams of Fe<sub>2</sub>P/gram of catalyst) of the sample (Table 1). For the bulk samples the actual  $S_g$  was employed, while for the supported samples it was calculated from the crystallite size using the equation  $S_g = 6/\rho D_c$ . The last factor,  $f$ , accounts for the loading of the active phase on the supported samples.

In all cases the experimental CO uptake was considerably smaller (average 6.6% for the bulk samples; average 20.5% for the fresh supported samples) than the theoretically expected metal site concentration (Table 3) for a clean surface. This indicates that possibly the surface is blocked by some species that prevents adsorption, such as phosphorus or unreduced oxygen. In the case of transition metal carbides it is found that oxygen uptakes are considerably higher than CO uptakes (42, 43), and this suggests that oxygen should be tried as a chemisorption probe.

The effect of the heating rate on the peak temperature ( $T_p$ ) associated with the reduction of supported catalysts (Fig. 9) was briefly examined in this work. The peak positions for water formation shifted to a temperature about 40–60 K higher as the heating rate ( $\beta$ ) was increased from 0.0167 (1 K min<sup>-1</sup>) to 0.0833 K s<sup>-1</sup> (5 K min<sup>-1</sup>). According to temperature-programmed reaction theory (44), the peak temperature ( $T_p$ ) is related to the heating rate ( $\beta$ ) and the apparent activation energy ( $E_a$ ) (Table 4) by the Redhead equation ( $2 \ln T_p - \ln \beta = E_a/RT_p + \text{Constant}$ ) (44). The activation energies found for Fe<sub>2</sub>P/silica, CoP/silica, and Ni<sub>2</sub>P/silica were 200, 220, and 150 kJ mol<sup>-1</sup>, respectively. The results here are comparable with the activation energy

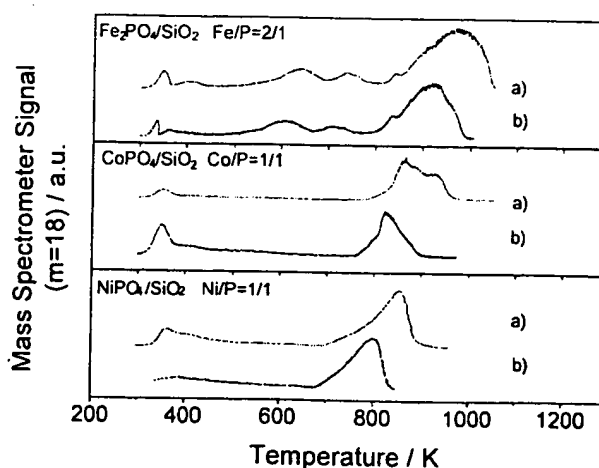


FIG. 9. TPR profiles of supported catalysts at different heating rates ( $\beta$ ). (a)  $\beta = 5$  K/min ( $0.08333 K s^{-1}$ ); (b)  $\beta = 1$  K/min ( $0.01667 K s^{-1}$ ).

TABLE 4

Apparent Activation Energy ( $E_a$ ) of Synthesis of the Supported Catalysts

Samples	$E_a$ (kJ mol <sup>-1</sup> )
Fresh 14 wt% Fe <sub>2</sub> P/silica	200
Fresh 9.4 wt% CoP/silica	220
Fresh 9.4 wt% Ni <sub>2</sub> P/silica	150

of oxygen diffusion in the corresponding metal oxides, FeO, CoO, and NiO, which are 126, 144, and 166 kJ mol<sup>-1</sup>, respectively, with preexponential factors of  $1.4 \times 10^{-2}$ ,  $2.15 \times 10^{-3}$ , and  $2 \times 10^{-4}$  cm<sup>2</sup> s<sup>-1</sup> (45). The correspondence is reasonable, as many solid state transformations are governed by diffusion processes (46).

#### Catalytic Activity in Hydroprocessing

Figures 10 and 11 present the HDS and HDN activities for the reactions of dibenzothiophene and quinoline, respectively. All three samples have high initial activities for HDS and HDN. However, except for the nickel sample in HDS, all catalysts undergo deactivation. The Fe<sub>2</sub>P/SiO<sub>2</sub> lost all HDS and HDN activity by 60 h, while the CoP/SiO<sub>2</sub> appeared to reach a baseline of about 32% HDS and 31% HDN at around 100 h. Only the Ni<sub>2</sub>P/SiO<sub>2</sub> had good, stable activity in HDS. The HDS sequence for the three samples was Ni<sub>2</sub>P/SiO<sub>2</sub> > CoP/SiO<sub>2</sub> > Fe<sub>2</sub>P/SiO<sub>2</sub>, while the HDN sequence was CoP/SiO<sub>2</sub> > Ni<sub>2</sub>P/SiO<sub>2</sub> > Fe<sub>2</sub>P/SiO<sub>2</sub>. Compared with a commercial Ni-Mo-S/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst at the same conditions (24), Ni<sub>2</sub>P/SiO<sub>2</sub> had a higher HDS activity, with 90 versus 76% conversion, but a lower HDN activity, with 14 versus 38% conversion. The measurements were made on the basis of equal chemisorption sites loaded in

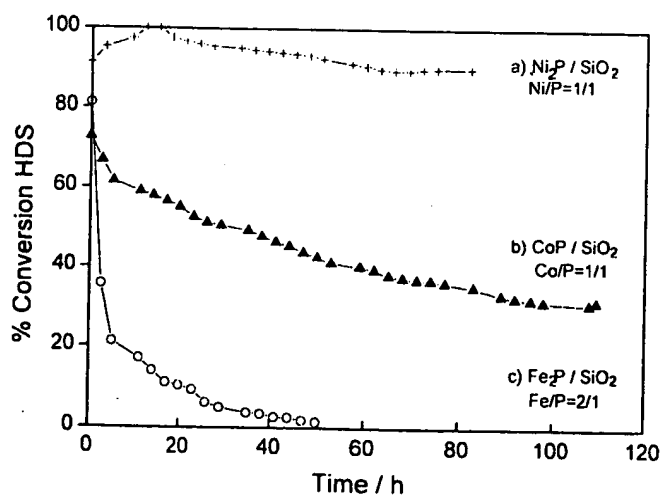


FIG. 10. Hydrodesulfurization performance of supported catalysts. (Basis: 35  $\mu$ mol of chemisorption sites).

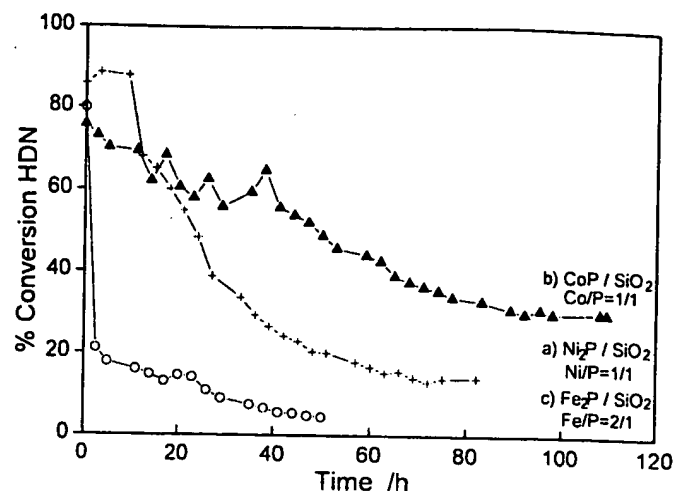


FIG. 11. Hydrodenitrogenation performance of supported catalysts. (Basis: 35  $\mu$ mol of chemisorption sites).

the reactor (35  $\mu$ mol for the phosphides, 33  $\mu$ mol for the sulfide). For the phosphides CO at room temperature was used for the chemisorption and for the sulfide O<sub>2</sub> at dry ice/acetone temperature was used. It may be that the CO chemisorption underestimates sites on the phosphide, so the conversions should be taken just as an approximation of intrinsic activity.

A listing of conversions and selectivities for all the reactions is provided in Table 5. For dibenzothiophene the only product observed was biphenyl. However, for quinoline a number of species were obtained, and these were categorized as HDN products and hydrogenation (HYD) products. For benzofuran, again only one product was obtained, ethylbenzene. The amount of benzofuran used was small (500 ppm) and the reaction is facile so is unlikely to interfere with the HDS and HDN reactions, as known from other studies with carbides, nitrides, and sulfides (47, 48). In the case of tetralin, at the reaction conditions the major species obtained was the dehydrogenation product naphthalene, although small amounts of *cis*- and *trans*-decalin were also observed.

Turnover rates and areal rates measured at the baseline levels are listed in Table 6. The basis of comparison is now 70  $\mu$ mol of sites, to make the numbers directly comparable to others published elsewhere (49). The procedure for conversion assumes a first-order reaction and is given in the footnotes of the table. The turnover rates are based on the experimentally determined CO uptakes on the fresh catalysts, while the areal rates are based on the calculated surface area of the phosphide crystallites using  $S_g = 6/\rho D_c$  and the weight loading factor  $f$ . The Fe<sub>2</sub>P catalyst deactivated completely and its rate is reported as zero. The CoP/SiO<sub>2</sub> had areal rates of  $1.4 \times 10^{15}$  mol m<sup>-2</sup> s<sup>-1</sup> in HDS and  $2.1 \times 10^{15}$  mol m<sup>-2</sup> s<sup>-1</sup> in HDN, while the Ni<sub>2</sub>P/SiO<sub>2</sub> had rates of  $3.4 \times 10^{15}$  mol m<sup>-2</sup> s<sup>-1</sup> in HDS and  $1.4 \times 10^{15}$  mol

TABLE 5

Product Distribution in Hydroprocessing<sup>a</sup>

Reactants	Type	Conversion (%)		Product	Selectivity (%)	
		Ni <sub>2</sub> P/SiO <sub>2</sub>	CoP/SiO <sub>2</sub>		Ni <sub>2</sub> P/SiO <sub>2</sub>	CoP/SiO <sub>2</sub>
Dibenzothiophene	HDS	90	32	Biphenyl	100	100
Quinoline	HDN	14	31	Propylcyclohexane	4	16
	HYD	44	49	Propylbenzene	9	9
				5,6,7,8-Tetrahydroquinoline	33	30
Benzofuran				Orthopropylaniline	31	23
				1,2,3,4-Tetrahydroquinoline	24	22
	HDO	35	11	Ethylbenzene	100	100
Tetralin	deHYD	31	6.5	Naphthalene	98.2	91.5
	HYD	0.6	0.6	trans-Decalin	0.6	3.6
				cis-Decalin	1.2	4.9

<sup>a</sup> Catalyst loaded was equivalent to 35  $\mu\text{mol}$  of CO uptake sites.

TABLE 6

## Rates of HDS and HDN of the Supported Catalysts

Sample	Turnover rate <sup>a</sup> ( $10^{-3} \text{ s}^{-1}$ )		Areal rate <sup>b</sup> ( $10^{15} \text{ mol m}^{-2} \text{ s}^{-1}$ )		Specific rate <sup>c</sup> ( $10^8 \text{ mol g}^{-1} \text{ s}^{-1}$ )		Volumetric rate <sup>d</sup> ( $10^9 \text{ mol cm}^{-3} \text{ s}^{-1}$ )	
	HDS	HDN	HDS	HDN	HDS	HDN	HDS	HDN
Fe <sub>2</sub> P/SiO <sub>2</sub>	0	0	0	0	0	0	0	0
CoP/SiO <sub>2</sub>	0.81	1.2	1.4	2.1	1.3	1.9	4.8	7.0
Ni <sub>2</sub> P/SiO <sub>2</sub>	1.5	0.60	3.4	1.4	2.2	0.9	8.1	0.33

<sup>a</sup> Calculated from  $r_t = QX/S$ , where  $Q$  is the molar rate of reactant,  $X$  is the conversion, and  $S$  is the mole of sites loaded. The basis used was 70  $\mu\text{mol}$ . Conversions were adjusted using the first-order formula  $X_2 = 1 - (1 - X_1)^{S_2/S_1}$ , where  $S_2/S_1 = 70 \mu\text{mol}/35 \mu\text{mol} = 2$ , and gave higher  $X$  than reported in Table 5 (CoP: HDS, 54%, HDN, 52%; Ni<sub>2</sub>P: HDS, 99%, HDN, 26%).

<sup>b</sup> Calculated from  $r_A = QXN_A/W S_g f$ , where  $N_A$  is Avogadro's number,  $W$  is the weight of catalyst,  $S_g$  is the metal phosphide surface area, and  $f$  is the fractional loading of phosphide.

<sup>c</sup> Calculated from  $r_s = r_t(\text{CO uptake})$ .

<sup>d</sup> Calculated from  $r_v = r_s \rho$ , where  $\rho$  is the apparent density of the catalysts,  $\sim 0.37 \text{ g cm}^{-3}$ .

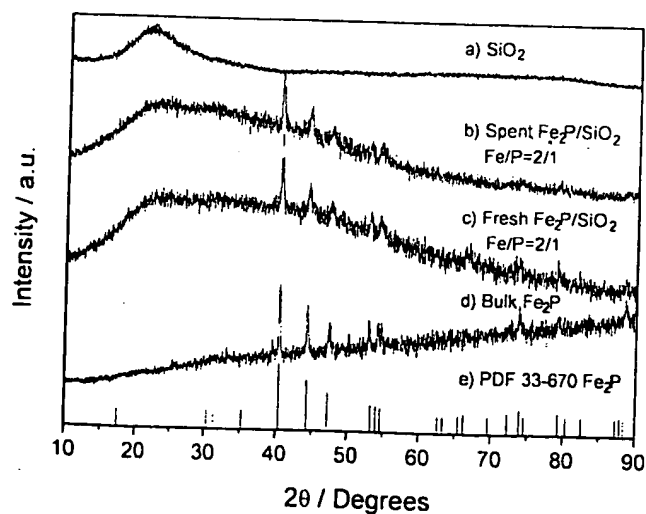


FIG. 12. X-ray diffraction patterns of iron phosphides and references. (a) Blank sample, SiO<sub>2</sub>; (b) spent sample, Fe<sub>2</sub>P/SiO<sub>2</sub>; (c) fresh sample, Fe<sub>2</sub>P/SiO<sub>2</sub>; (d) bulk sample, Fe<sub>2</sub>P; and (e) PDF 33-670 Fe<sub>2</sub>P (Ref. 41).

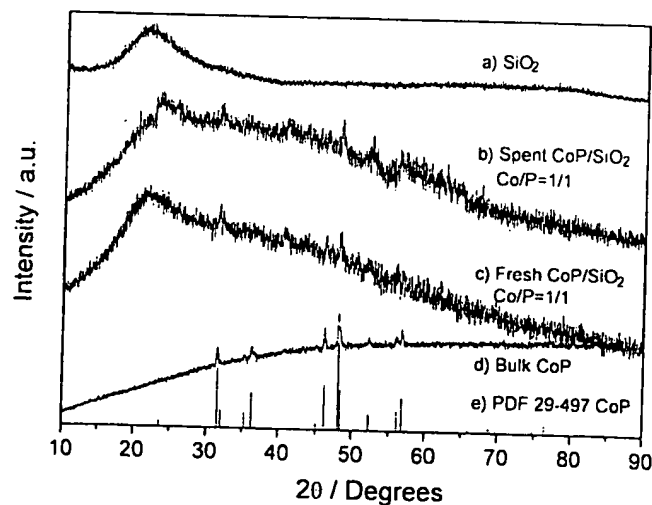


FIG. 13. X-ray diffraction patterns of cobalt phosphides and references. (a) Blank sample, SiO<sub>2</sub>; (b) spent sample, CoP/SiO<sub>2</sub>; (c) fresh sample, CoP/SiO<sub>2</sub>; (d) bulk sample, CoP; and (e) PDF 29-497 CoP (Ref. 41).

$\text{m}^{-2} \text{s}^{-1}$  in HDN. In a recent study of the HDN on unsupported samples Stinner *et al.* report areal rates of  $4.8 \times 10^{16} \text{ mol m}^{-2} \text{s}^{-1}$  on  $\text{Co}_2\text{P}$  and  $5.8 \times 10^{16} \text{ mol m}^{-2} \text{s}^{-1}$  on  $\text{Ni}_2\text{P}$  (26). The higher HDN rates on those samples can be attributed to several factors. First, Stinner *et al.* studied only HDN and employed a more reactive substrate (*o*-propylaniline rather than quinoline), which probably led to higher rates. They also carried out their tests without using sulfur compounds in the feed. Sulfur compounds can lead to competitive adsorption and lower rates. Finally, Stinner *et al.* used low-surface-area ( $1\text{--}3 \text{ m}^2 \text{g}^{-1}$ ) unsupported materials in a low-conversion regime, which would tend to result in higher rates. Nevertheless, despite the differences in experimental conditions the rates are of similar orders of magnitude.

The XRD patterns of the silica support, fresh phosphide samples, spent samples, and PDF references are compared in Figs. 12–14. These results show that silica did not influence the phases of the phosphides formed, which were the same as those obtained in the bulk materials  $\text{Fe}_2\text{P}$ ,  $\text{CoP}$ , and  $\text{Ni}_2\text{P}$ . The XRD patterns for the spent iron and cobalt samples were unchanged from the corresponding fresh samples, which shows that the  $\text{Fe}_2\text{P}$  phase (Fig. 12) and  $\text{CoP}$  phase (Fig. 13) are stable during the hydrotreating reaction. For the spent nickel sample, one more peak was observed (Fig. 14). Comparing this pattern with those of other nickel phosphide compounds, it was found that the peak (\*) matched one due to  $\text{Ni}_{12}\text{P}_5$ . This indicated that possibly a part of the  $\text{Ni}_2\text{P}$  phase transformed to a  $\text{Ni}_{12}\text{P}_5$ -like phase during hydrotreating. XPS measurement for this sample (Table 7) showed a P/Ni ratio close to 1 for the fresh sample, which decreased to 0.77 for the spent catalyst. This decrease may be related to the drop in HDN activity for this sample. The XPS analysis surprisingly also indicated a lack of S or N on the spent sample. The measurements were repeated on samples treated in He (just to remove volatile compounds), but the results were the same. This is likely due to lack of sensitivity by XPS at the levels expected for surface sulfur species in these supported samples. Already the signals for Ni and P were very low.

The results of posthydrotreating characterization are also presented in Table 3. For the iron sample, the CO uptake decreased to zero after the hydrotreating. The loss of the CO uptake is likely associated with the dramatic deactivation

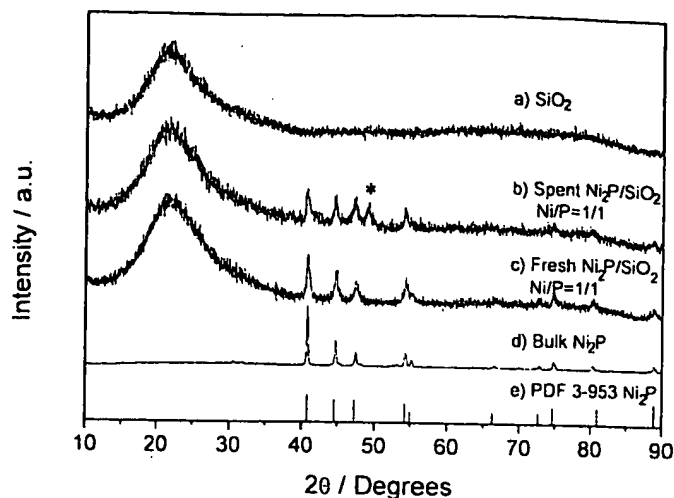


FIG. 14. X-ray diffraction patterns of nickel phosphides and references (a) Blank sample- $\text{SiO}_2$ ; (b) spent sample  $\text{Ni}_2\text{P}/\text{SiO}_2$ ; (c) fresh sample  $\text{Ni}_2\text{P}/\text{SiO}_2$ ; (d) bulk sample  $\text{Ni}_2\text{P}$ ; and (e) PDF 3-953  $\text{Ni}_2\text{P}$  (Ref. 41).

tion of the iron sample (Figs. 10c and 11c). As to the spent cobalt sample, the CO uptake also decreased substantially, but not to zero, as in the case of the iron sample. This was in line with the less complete deactivation of the catalyst. In the case of nickel, again a decrease in CO uptake was observed, but the decrease was much smaller than those of the iron and cobalt samples. Overall, the trend appears to indicate that the decrease in catalytic performance is related to the loss of active sites.

The reduction in the number of active sites is apparently caused by sulfidation of the catalysts. This is currently being investigated by extended X-ray absorption spectroscopy (EXAFS) of the fresh and spent samples (49). The results indicate that the catalysts are phase pure and sulfidation is restricted to the surface of the phosphide crystallites, as X-ray diffraction analysis shows that the phosphide phase is retained. The surface sulfidation process appears to be more pronounced in iron and cobalt phosphide, which show considerable deactivation in HDS and HDN. The nickel phosphide appears to be more tolerant to sulfur and thus retains high HDS activity. This is entirely reproducible. Its HDN activity is lowered, probably because the latter reaction is structure sensitive (49), and the site requirements for nitrogen removal are disrupted.

TABLE 7  
XPS Results for Supported Nickel Samples

Fresh 9.4 wt % $\text{Ni}_2\text{P}/\text{silica}$	Element	C 1s	O 1s	N 1s	S 2p	P 2p	Ni 2p	Si 2p
	Concentration (%)	16.73	55.42	0	0	0.80	0.83	26.22
Spent 9.4 wt % $\text{Ni}_2\text{P}/\text{silica}$	Element	C 1s	O 1s	N 1s	S 2p	P 2p	Ni 2p	Si 2p
	Concentration (%)	19.24	53.16	0	0	0.36	0.47	26.77

## CONCLUSIONS

Pure  $\text{Fe}_2\text{P}$ ,  $\text{CoP}$ , and  $\text{Ni}_2\text{P}$  phases were successfully synthesized by means of temperature-programmed reduction of the corresponding phosphates. The silica-supported forms of these samples were also successfully prepared, with retention of the active phase and increased CO uptake and BET surface area. It was found that  $\text{Fe}_2\text{P}/\text{SiO}_2$  had good initial activity for HDS of dibenzothiophene and HDN of quinoline, but that this activity fell to zero in about 60 h. The  $\text{CoP}/\text{SiO}_2$  catalyst also deactivated but appeared to reach a stable baseline of 32% HDS and 31% HDN conversion. Only the  $\text{Ni}_2\text{P}/\text{SiO}_2$  had a stable and high conversion in HDS of 90%, although its HDN was low at 14%. The deactivation in all cases was associated with a decrease in the number of surface metal sites as titrated by the chemisorption of CO. For the most promising catalyst,  $\text{Ni}_2\text{P}/\text{SiO}_2$ , HDS was higher than that of a commercial catalyst,  $\text{Ni-Mo-S}/\gamma\text{-Al}_2\text{O}_3$ , based on equal sites loaded in the reactor, as measured by CO uptake for the phosphide and low-temperature  $\text{O}_2$  chemisorption for the sulfide. The development and improvement of this group of phosphides in the hydroprocessing field is a promising area of research.

## ACKNOWLEDGMENTS

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# Transition Metal Compounds

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## Crystallographic and Magnetic Properties of Solid Solutions of the Phosphides $M_2P$ , $M = \text{Cr, Mn, Fe, Co, and Ni}$

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Several phosphides with the chemical formula  $M_2P$  crystallize in a hexagonal structure:  $\text{Mn}_2\text{P}$ ,  $\text{Fe}_2\text{P}$ , and  $\text{Ni}_2\text{P}$ . The structure of  $\text{Co}_2\text{P}$  is orthorhombic. These two structures are related via an identical elementary subcell consisting of a tetrahedral-site and a pyramidal-site  $M$ -atom pair. This investigation shows that solid solutions between two hexagonal end members, such as  $\text{Fe}_2\text{P}$  or  $\text{Ni}_2\text{P}$  with  $\text{Mn}_2\text{P}$ , may exhibit orthorhombic structures at intermediate compositions.  $\text{Fe}_2\text{P}$  shows complete solid solubility with  $\text{Ni}_2\text{P}$ . Curiously, hexagonal and orthorhombic symmetries alternate with decreasing number of 3d electrons,  $\text{Ni}_2\text{P}(\text{hex})-\text{Co}_2\text{P}(\text{ortho})-\text{Fe}_2\text{P}(\text{hex})-\text{FeMnP}(\text{ortho})-\text{Mn}_2\text{P}(\text{hex})$ . Lattice parameter variations with composition and Mössbauer studies reveal atomic ordering in the mixed systems, Mn and Cr substituting for pyramidal-site iron in  $\text{FeMnP}$  and  $\text{FeCrP}$  while Ni and Co substitute preferentially for tetrahedral-site iron in  $\text{FeCoP}$  and  $\text{FeNiP}$ . While neither  $\text{Co}_2\text{P}$  nor  $\text{Mn}_2\text{P}$  are ferromagnetic, intermediate phases are, the Curie temperature and magnetization reaching the maximum values  $310^\circ\text{C}$  and  $3.03 \mu_B/\text{molecule}$  for  $\text{MnCoP}$ . Metamagnetism appears for a range of compositions about  $(\text{Mn}_{0.7}\text{Co}_{0.3})_2\text{P}$ . The  $\text{Co}_2\text{P}-\text{Fe}_2\text{P}$  system is also ferromagnetic with a maximum Curie temperature near  $\text{FeCoP}$ . This system shows a sharp discontinuity in magnetization, but only a small discontinuity in Curie temperature, across the phase transition. Sensitivity to stoichiometry in the magnetization of  $\text{Fe}_{2-x}\text{P}$  is attributed to an electron/atom ratio near that for the appearance of metamagnetism.

### I. INTRODUCTION

Several phosphides of the first-row transition metals are ferromagnetic: for example,  $\text{Fe}_2\text{P}$ ,<sup>1,2</sup>  $\text{Fe}_3\text{P}$ ,<sup>1,3,4</sup> and  $\text{MnP}$ .<sup>5</sup> Near  $50^\circ\text{K}$ ,  $\text{MnP}$  exhibits an antiferromagnetic to ferromagnetic transition,<sup>6-11</sup> the antiferromagnetic phase consisting of two parallel helices.<sup>11,12</sup> Other phosphides, such as  $\text{Mn}_3\text{P}$ <sup>13</sup> and  $\text{Mn}_2\text{P}$ ,<sup>14</sup> are antiferromagnetic.

Studies of  $\text{MnP}-\text{FeP}$  solid solutions show that  $\text{FeP}$  is not ferromagnetic even at very low ( $1.5^\circ\text{K}$ ) temperatures.<sup>3,4,15-18</sup>  $\text{MnP}-\text{MnAs}$  solid solutions are magnetically complex, exhibiting several magnetic tran-

sitions.<sup>19-23</sup> Substitutions of boron for phosphorous in  $\text{Fe}_2\text{P}$ <sup>24,25</sup> have shown that the metalloid electrons are donors to the 3d bands of iron, whereas substitutions of chromium,<sup>26</sup> nickel or cobalt<sup>13,27</sup> give changes of magnetization with composition similar to those found<sup>18,28</sup> for the borides  $M_2\text{B}$  and  $\text{MB}$ .

This work is concerned with the magnetic properties of solid solutions of phosphides of the type  $M_2P$ . Nowotny and Henglein<sup>30</sup> have presented a brief structural survey of a few solid solutions among  $M_2P$  phosphides. Not all the phosphides  $M_2P$  have the same crystal structure<sup>30-33</sup>; some, like  $\text{Mn}_2\text{P}$  and  $\text{Ni}_2\text{P}$ , are

<sup>1</sup> H. Le Chatelier and S. Wologdine, *Compt. Rend.* **149**, 709 (1909).

<sup>2</sup> J. L. Haughton, *J. Iron Steel Inst.* **115**, 417 (1927).

<sup>3</sup> Shu Chiba, *J. Phys. Soc. Japan* **15**, 581 (1960).

<sup>4</sup> A. J. P. Meyer and M. C. Cadeville, *J. Phys. Soc. Japan* **17**, 223 (1962).

<sup>5</sup> K. H. Sweeny and A. B. Scoot, *J. Chem. Phys.* **22**, 917 (1954).

<sup>6</sup> B. F. Stein and R. H. Walmsley, *Phys. Rev.* **148**, 933 (1966).

<sup>7</sup> G. P. Felchert, *J. Appl. Phys.* **37**, 1056 (1966).

<sup>8</sup> J. Komatsubara, K. Kinoshita, and E. Hirahara, *J. Phys. Soc. Japan* **20**, 2036 (1965).

<sup>9</sup> A. Roger and R. Fruchart, *Compt. Rend.* **264**, 508 (1967).

<sup>10</sup> E. E. Hubert Jr. and D. H. Ridgley, *Phys. Rev.* **135**, 1099 (1964).

<sup>11</sup> J. B. Forsyth, S. J. Pickart, and P. J. Brown, *Proc. Phys. Soc.* **88**, 333 (1966).

<sup>12</sup> S. Takeuchi and K. Motizuki, *J. Phys. Soc. Japan* **24**, 742 (1967).

<sup>13</sup> R. J. Gambino, T. P. McGuire, and Y. Nakamura, *J. Appl. Phys.* **38**, 1253 (1967).

<sup>14</sup> M. Yessik, *Phil. Mag.* **17**, 623 (1968).

<sup>15</sup> M. C. Cadeville, *thèse*, Strasbourg (1965), p. 29.

<sup>16</sup> A. Gerard, *Bull. Soc. Belg. Phys.* **5**, 43 (1966).

<sup>17</sup> J. Bonnerot, R. Fruchart, and A. Roger, *Phys. Letters* **26A**, 536 (1968).

<sup>18</sup> R. E. Bailey and J. F. Duncan, *Inorg. Chem.* **6**, 1444 (1966).

<sup>19</sup> J. B. Goodenough, D. H. Ridgley, and W. A. Newman, in *Proc. Intern. Conf. Mag., Nottingham* (1964).

<sup>20</sup> D. H. Ridgley and J. H. Geisman, *J. Appl. Phys.* **39**, 592 (1968).

<sup>21</sup> H. Ido and T. Suzuki, *J. Phys. Japan* **24**, 964 (1968).

<sup>22</sup> R. M. Rosenberg, W. H. Cloud, F. J. Darnell, and R. B. Flippin, *Phys. Letters* **25A**, 723 (1967).

<sup>23</sup> A. Roger and R. Fruchart, *Mat. Res. Bull.* **3**, 253 (1968).

<sup>24</sup> E. Fruchart, A. M. Triquet, and R. Fruchart, *Ann. Chim.* **9**, 323 (1964).

<sup>25</sup> R. Fruchart, A. M. Blanc, E. Fruchart, J. P. Bouchaud, and J. P. Senateur, *Colloque International No. 157 du C.N.R.S.* (1965), p. 95.

<sup>26</sup> A. M. Blanc, E. Fruchart, and R. Fruchart, *Ann. Chim.* **2**, 251 (1967).

<sup>27</sup> A. M. Blanc, E. Fruchart, and R. Fruchart (unpublished).

<sup>28</sup> M. C. Cadeville and A. J. P. Meyer, *Compt. Rend.* **255**, 339 (1962).

<sup>29</sup> M. C. Cadeville, E. Daniel, and A. J. P. Meyer, *Colloque International No. 157 du C.N.R.S.* (1965), p. 361.

<sup>30</sup> H. Nowotny and E. Henglein, *Monats. Chem.* **79**, 385 (1948).

<sup>31</sup> S. Rundqvist and F. Jellinek, *Acta Chem. Scand.* **13**, 425 (1959).

<sup>32</sup> O. Arstad and H. Nowotny, *Z. Physik. Chem.* **B38**, 356 (1937).

<sup>33</sup> H. Nowotny and E. Henglein, *Z. Physik. Chem.* **B40**, 281 (1938).

isomorphous with hexagonal  $\text{Fe}_2\text{P}$ <sup>31,32</sup> and others have the orthorhombic structure<sup>34</sup> of  $\text{Co}_2\text{P}$ . The structure of  $\text{Cr}_2\text{P}$  has not yet been determined. Rundquist<sup>35</sup> has discussed the similarities between the hexagonal and orthorhombic phosphides. In order to relate magnetic properties to crystal structure, we review briefly this similarity here, emphasizing the metalloid environment of the metal atoms and the elementary structural unit common to both structures.

Along the  $[001]$  direction of the hexagonal structure or the  $[010]$  direction of the orthorhombic structure, phosphorous atoms form, alternately, tetrahedra and square-based pyramids, as shown in Fig. 1(a), making a canal of triangular cross section. Occupation of both tetrahedral and pyramidal sites cannot occur simultaneously along the same canal. Consequently, two

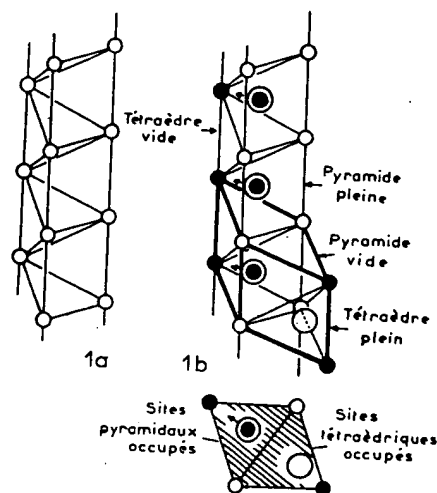


FIG. 1. Building blocks of hexagonal and orthorhombic  $M_2\text{P}$  structures. (a) Phosphorous canals. (b) Relationship of pyramidal-site and tetrahedral-site atoms forming a rhombohedral subcell.

kinds of canals are possible: one has only tetrahedral sites occupied, the other only pyramidal sites occupied. In both the hexagonal  $\text{Fe}_2\text{P}$  and orthorhombic  $\text{Co}_2\text{P}$  structures, canals of different type share common pyramidal square bases to form canal pairs. This pairing creates a sequence of elementary structural units along the paired canals. As shown in Fig. 1(b), these units are rhombohedral and consist of an occupied tetrahedron-occupied pyramid pair, and an empty-tetrahedron-empty-pyramid pair. The hexagonal  $\text{Fe}_2\text{P}$  structure of Fig. 2 corresponds to an hexagonal assembly of these canal pairs whereas the orthorhombic  $\text{Co}_2\text{P}$  structure of Fig. 3 results from a zig-zag stacking.

## II. SAMPLE PREPARATION

Solid solutions were prepared at temperatures between  $850^\circ$  and  $900^\circ\text{C}$  in evacuated, sealed silica amp-

<sup>31</sup> H. Nowotny, Z. Anorg. Chem. 254, 31 (1947).

<sup>32</sup> S. Rundqvist, Arkiv für Kemi 20, 7 (1962).

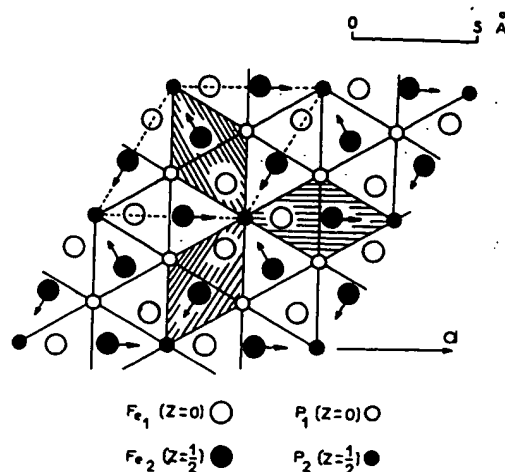


FIG. 2. Arrangement of rhombohedral subcells in hexagonal  $\text{Fe}_2\text{P}$  structure.

pules by solid-phase diffusion of phosphides prepared by a previously described method.<sup>9</sup>

## III. EXPERIMENTAL METHODS

1. *X-ray diffraction*: Diffraction patterns were taken with a Seeman-Bohlin camera with monochromatic chromium  $K\alpha_1$  radiation. The precision of the measurements is about  $10^{-3}$  Å.

2. *Magnetic analysis*: Curie and magnetic-transition temperatures were determined with a thermomagnetic balance from  $77^\circ$ – $1400^\circ\text{K}$  in fields of a few hundred Oersteds. Magnetic moments were obtained in fields up to 26.6 kOe and in temperatures down to  $20.4^\circ\text{K}$ .

3. *Mössbauer spectra*: The apparatus includes a  $\text{Co}^{57}$  source imbedded in palladium and placed in a parabolic-movement vibrator having a parabolic displacement. The spectra, obtained from  $90^\circ$  to  $650^\circ\text{K}$ , were recorded in a four-hundred-channel analyzer. Zone-melted iron was used as a standard.

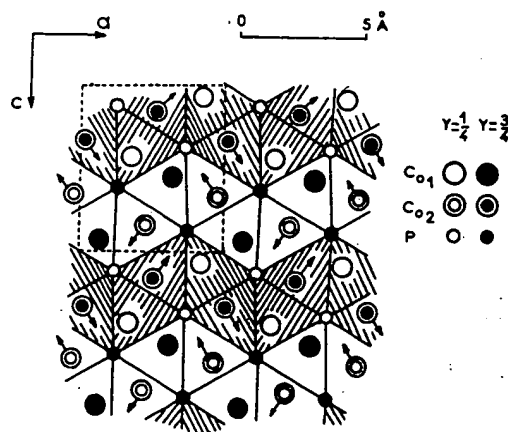


FIG. 3. Arrangement of rhombohedral subcells in orthorhombic  $\text{Co}_2\text{P}$  structure.

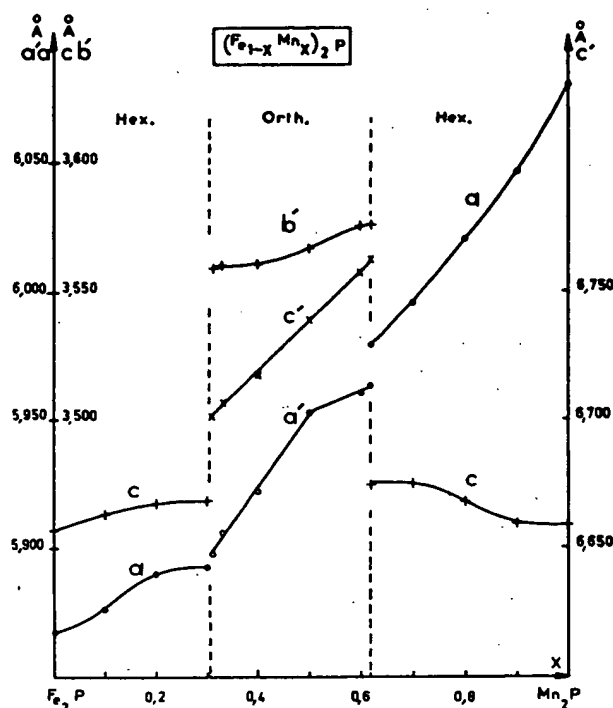


FIG. 4. Lattice parameters and structural homogeneity ranges for the system  $(\text{Fe}_{1-x}\text{Mn}_x)_2\text{P}$ .

#### IV. CRYSTALLOGRAPHIC STUDY

##### A. Systems with Three Single-Phase Regions

1.  $(\text{Fe}_{1-x}\text{Mn}_x)_2\text{P}$ : The solid-solution system  $(\text{Fe}_{1-x}\text{Mn}_x)_2\text{P}$  has orthorhombic symmetry in the intermediate compositional range  $0.31 \leq x \leq 0.62$  (Fig. 4). The orthorhombic and hexagonal phases are separated by very narrow two-phase regions, and the limiting compositions are very slightly dependent on the temperature of sample preparation. Lattice parameters do not obey Vegard's law, and abrupt changes in  $a'$  occur at  $x=0.5$ , or  $\text{MnFeP}$ . The hexagonal phase is more dense than the orthorhombic phase ( $107.58 \text{ Å}^3$  vs  $108.19 \text{ Å}^3$  for  $x=0.62$ ).

2.  $(\text{Mn}_{1-x}\text{Ni}_x)_2\text{P}$ : This system is similarly characterized by orthorhombic structures in the intermediate compositional range  $0.20 \leq x \leq 0.50$ .

3.  $(\text{Fe}_{1-x}\text{Cr}_x)_2\text{P}$ : This system has orthorhombic structures in the compositional range  $0.15 \leq x \leq 0.55$ , and the rate of change with  $x$  of all three orthorhombic parameters  $a'$ ,  $b'$ ,  $c'$ , show anomalous changes at  $x=0.50$ . However, for  $x > 0.60$  the system is multiphase.

##### B. Systems with Two Single-Phase Regions

1.  $(\text{Co}_{1-x}\text{Fe}_x)_2\text{P}$ : In this system hexagonal structures are restricted to the relatively narrow compositional range  $x > 0.84$  (Fig. 5). Here the limiting compositions of the very narrow two-phase region, of width  $\Delta x$ , vary with thermal treatment:  $\Delta x \approx 0.01$ ,

0.04 for preparation at  $600^\circ$  and  $950^\circ\text{C}$ , respectively. Vegard's law is not obeyed, and  $c'$  vs  $x$  shows an inflection point near  $x=0.60$ . To obtain a unique phase at  $850^\circ\text{C}$ , it was necessary to add an excess of 3 at.% phosphorous throughout the range  $x < 0.50$ .

2.  $(\text{Co}_{1-x}\text{Mn}_x)_2\text{P}$ : Hexagonal structures in this system are restricted to the compositional range  $x > 0.80$  (Fig. 6). Particularly marked anomalies in  $a'$  and  $b'$  occur at the composition  $\text{MnCoP}$ .

3.  $(\text{Mn}_{1-x}\text{Cr}_x)_2\text{P}$ : Substitution of 10 at.% chromium into  $\text{Mn}_2\text{P}$  is sufficient to make the hexagonal structure disappear. For  $x \geq 0.10$ , the system is multiphase.

4.  $(\text{Co}_{1-x}\text{Ni}_x)_2\text{P}$ : In this system, hexagonal structures are found over most of the compositional range, orthorhombic structures being restricted to the range  $x \leq 0.15$ . The hexagonal  $c$  parameter has a broad minimum at  $x=0.65$ .

#### C. Complete Solid Solutions

The hexagonal system  $(\text{Fe}_{1-x}\text{Ni}_x)_2\text{P}$  has complete solid solutions. The lattice parameters vary anomalously with  $x$  (Fig. 7), the most accentuated changes occurring at the composition  $x=0.85$ , which has the minimum volume.

#### V. MAGNETIC STUDY

1.  $(\text{Co}_{1-x}\text{Mn}_x)_2\text{P}$ : Although the binary compounds  $\text{Mn}_2\text{P}$  and  $\text{Co}_2\text{P}$  are not ferromagnetic, the orthorhombic domain of the system  $(\text{Co}_{1-x}\text{Mn}_x)_2\text{P}$  contains a large

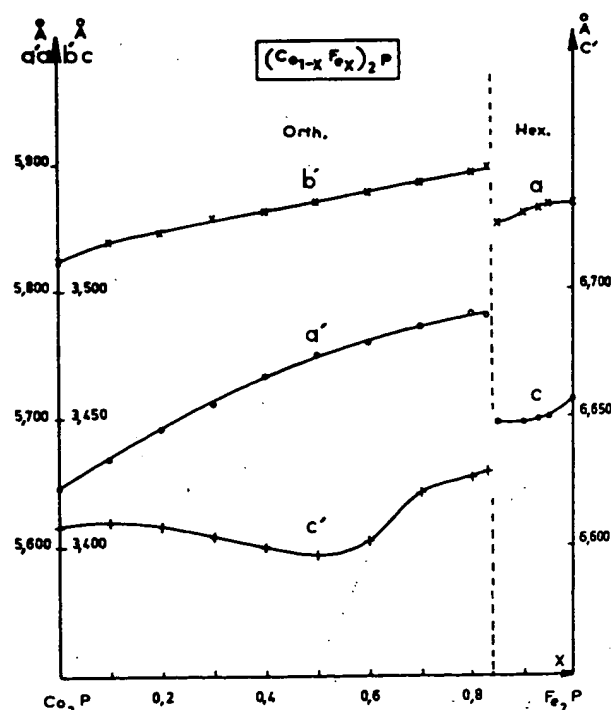


FIG. 5. Lattice parameters and structural homogeneity ranges for the system  $(\text{Co}_{1-x}\text{Fe}_x)_2\text{P}$ .



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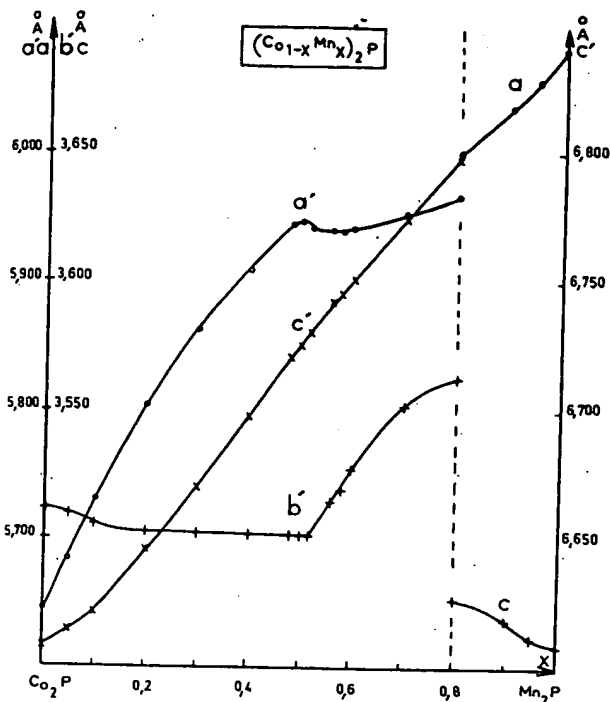


FIG. 6. Lattice parameters and structural homogeneity ranges for the system  $(\text{Co}_{1-x}\text{Mn}_x)_2\text{P}$ .

ferromagnetic compositional region (Fig. 8). The Curie temperatures  $T_c$  vary rapidly with  $x$ , exhibiting a sharp maximum of 583°K at  $x=0.5$  ( $\text{CoMnP}$ ). In the interval  $0.56 \leq x \leq 0.66$ , there is a metamagnetic to ferromagnetic transition with increasing temperature.

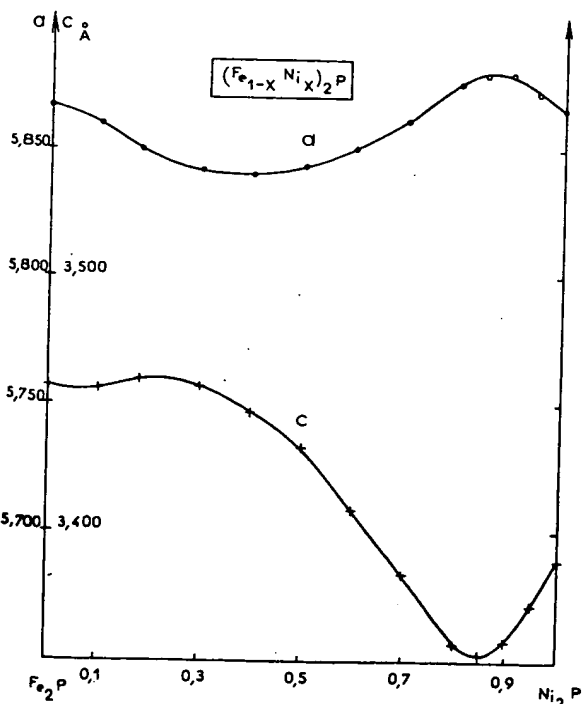


FIG. 7. Lattice parameters for the system  $(\text{Fe}_{1-x}\text{Ni}_x)_2\text{P}$ .

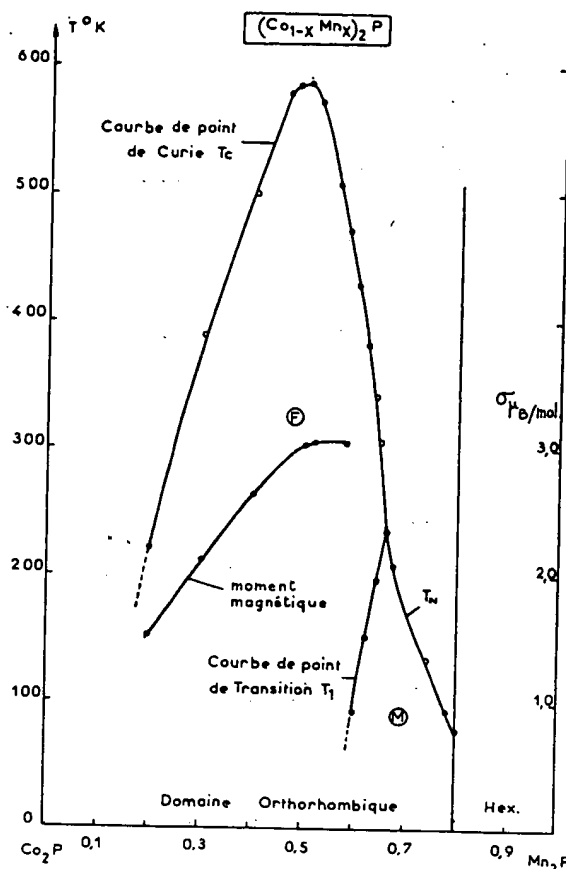


FIG. 8. Magnetic transition temperatures and magnetization at 0°K for the system  $(\text{Co}_{1-x}\text{Mn}_x)_2\text{P}$ .

The transition temperature  $T_1$  increases rapidly with  $x$  while  $T_c$  decreases, the domain of ferromagnetism in weak external fields terminating at  $x=0.66$ .  $T_1$  varies strongly with applied field (Figs. 9-11), and for  $x \geq 0.66$  the magnetic order-disorder transition is a Néel temperature  $T_N$  (Figs. 8-10). The saturation magnetiza-

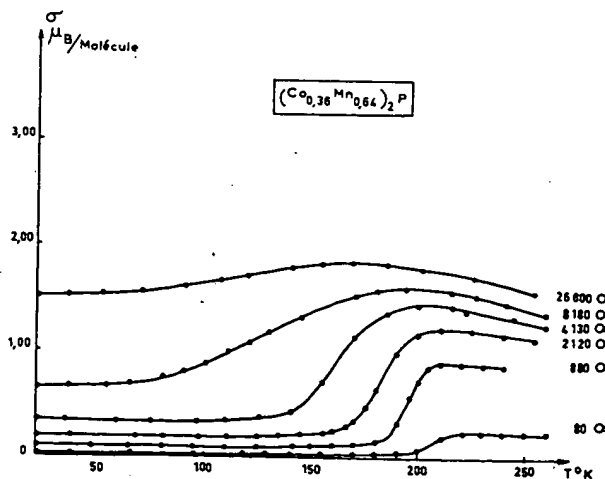
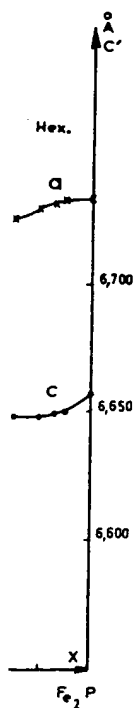


FIG. 9. Thermomagnetic curves at various applied field strengths for  $(\text{Co}_{0.38}\text{Mn}_{0.62})_2\text{P}$ .

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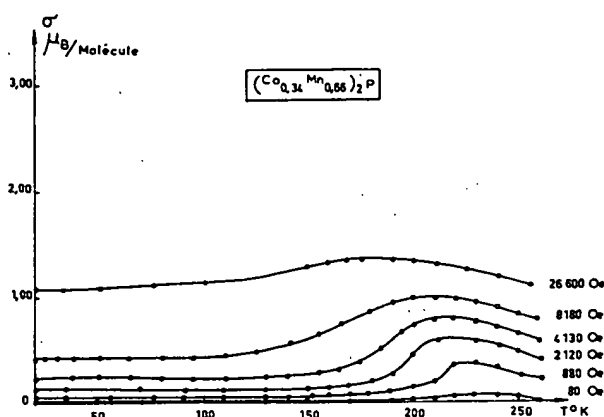


FIG. 10. Thermomagnetic curves at various applied field strengths for  $(\text{Co}_{0.34}\text{Mn}_{0.66})_2\text{P}$ .

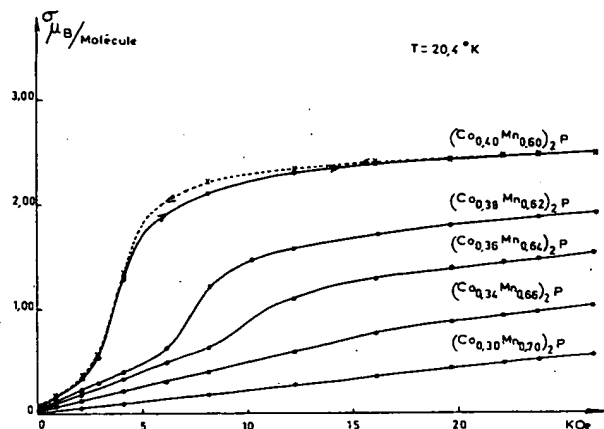


FIG. 11. Magnetization curves at 20.4°K for various compositions  $(\text{Co}_{1-x}\text{Mn}_x)_2\text{P}$  that are metamagnetic at low temperatures.

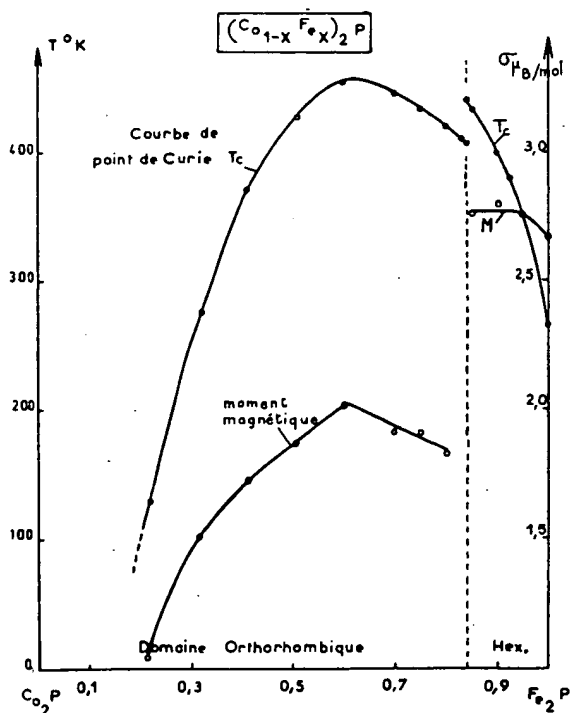


FIG. 12. Curie temperature and magnetization at 0°K for the system  $(\text{Co}_{1-x}\text{Fe}_x)_2\text{P}$ .

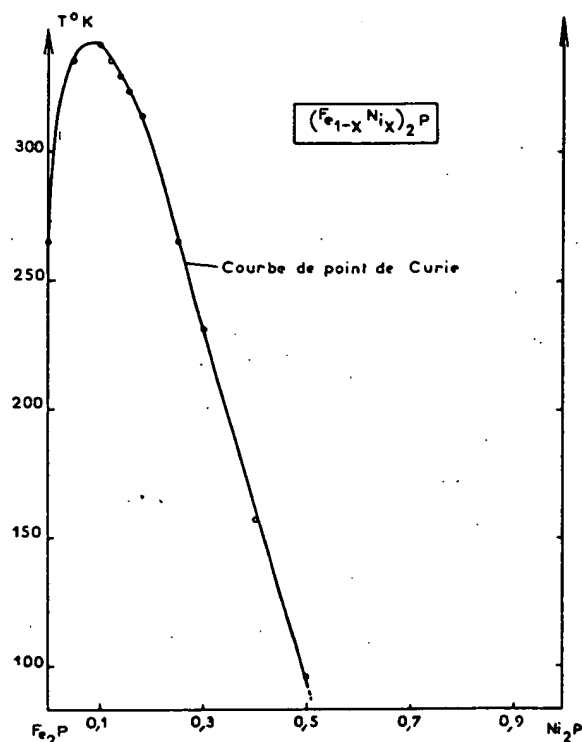


FIG. 13. Curie temperature for the system  $(\text{Fe}_{1-x}\text{Ni}_x)_2\text{P}$ .

tion, extrapolated to 0°K, is also shown in Fig. 8. It reaches a maximum of  $3.06 \mu_B/\text{molecule}$  at  $x \approx 0.55$ .

2.  $(\text{Co}_{1-x}\text{Fe}_x)_2\text{P}$ : As in the previous system, the Curie temperature  $T_c$  rises rapidly with  $x$  to a maximum of 459°K at  $x=0.62$  (Fig. 12). However, here there is no metamagnetic state, and there is a discontinuity in  $T_c$  at  $x=0.84$ , where the structural change occurs, from 407°–441°K. Since thermomagnetic analysis of samples with  $x \leq 0.50$  revealed the presence of a magnetic impurity (the amount increasing with preparation temperature) having a Curie temperature slightly less than that of pure cobalt, for  $x \leq 0.50$ , the phosphorous content was systematically increased by 3 at. % in these

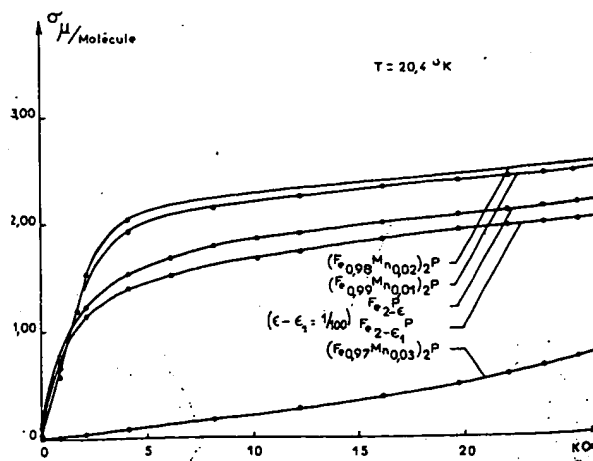


FIG. 14. Magnetization vs applied field at 20.4°K of  $\text{Fe}_2\text{P}$  and  $\text{Fe}_2\text{P}:\text{Mn}$ .

compositions in order to obtain single magnetic phases. The magnetization (Fig. 12) decreases abruptly from 2.75 to 1.83  $\mu_B$ /molecule on passing from the hexagonal to the orthorhombic phase, and within the orthorhombic phase it reaches a maximum of 2.02  $\mu_B$ /molecule at  $x=0.60$ .

3.  $(\text{Fe}_{1-x}\text{Ni}_x)_2\text{P}$ : Substitution of Ni into  $\text{Fe}_2\text{P}$  produces a similar sharp increase in  $T_c$  (Fig. 13), which reaches a maximum of 342°K at  $x=0.08$ , decreasing rapidly with larger  $x$  to less than 100°K at  $x=0.50$ . The saturation magnetization has not yet been measured.

4.  $(\text{Fe}_{1-x}\text{Mn}_x)_2\text{P}$ : Very small substitutions of manganese into  $\text{Fe}_2\text{P}$  induce metamagnetism. By  $x=0.03$ , the antiferromagnetic state is stable in fields up to 26.6 kOe (see Fig. 14). Similar changes occur with chromium substitutions.

5.  $\text{Fe}_{2-x}\text{P}$ : Cadeville and Meyer<sup>15</sup> have reported variations in magnetization with deviations from stoichiometry as large as 2.76  $\mu_B$ /molecule for  $\text{Fe}_2\text{P}$  to 2.14  $\mu_B$ /molecule for  $\text{Fe}_{2-x}\text{P}$ . Similarly, we find that two single-phase samples of nominal compositions ( $\text{Fe}_2\text{P}$ ), but differing by one weight percent iron, have magnetizations of 2.67  $\mu_B$  and 2.44  $\mu_B$ /molecule.

## VI. MÖSSBAUER SPECTRA

### A. Studies in the Paramagnetic State

The Mössbauer spectrum of  $\text{Fe}_2\text{P}$  has already been studied.<sup>16,18</sup> Pyramidal-site iron atoms are subject to a significant electric-field gradient that splits the resonance line by  $\approx 0.4$  mm/sec. The tetrahedral-site iron

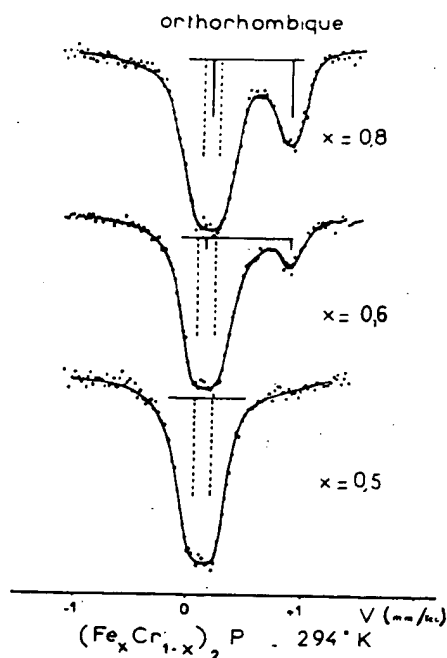


FIG. 15. Mössbauer spectra of  $(\text{Fe}_x\text{Cr}_{1-x})_2\text{P}$  in the paramagnetic state.

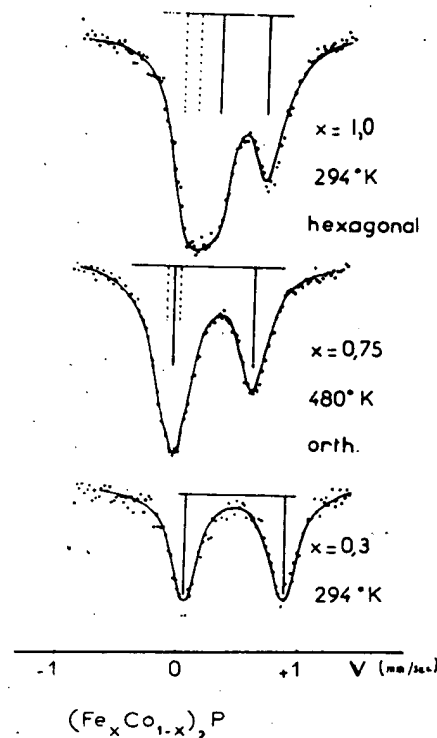


FIG. 16. Mössbauer spectra of  $(\text{Fe}_x\text{Co}_{1-x})_2\text{P}$  in the paramagnetic state.

atoms exhibit a single resonance line of enlarged width, probably reflecting a slight deformation of the tetrahedron. Therefore, Mössbauer studies of  $(\text{Fe}_{1-x}\text{M}_x)_2\text{P}$  systems permit a direct determination of the site preferences of the solute  $M$  atoms.

1.  $M = \text{Mn or Cr}$ : Changes with  $x$  in the Mössbauer spectra indicate a total substitution of manganese and chromium atoms for pyramidal-site iron. Only the single line with enlarged width remains in the spectra of  $\text{FeMnP}$  and  $\text{FeCrP}$  (Fig. 15).

2.  $M = \text{Co or Ni}$ : Cobalt and nickel substitute preferentially for tetrahedral-site iron. About 15% of the cobalt atoms occupy pyramidal sites in  $\text{FeCoP}$ . For  $x > 0.70$ , only the symmetric doublet, separated by 0.83 mm/sec, appears in the spectrum (Fig. 16). About 25% of the nickel atoms occupy pyramidal sites in  $\text{FeNiP}$ .

### B. Studies in the Ferromagnetic State

The spectra of the system  $(\text{Fe}_{1-x}\text{Co}_x)_2\text{P}$  at  $T = 294^\circ\text{K} < T_c$  for a series of compositions in the range  $0 < x < 0.25$  vary regularly with  $x$  and show little change on passing from hexagonal to orthorhombic symmetry. They have been interpreted with the method of Wertheim,<sup>16</sup> where the parameters to be determined are the internal fields at the tetrahedral-site and pyramidal-site nuclei  $H_n^t$  and  $H_n^p$ , the quadrupolar field strengths  $\frac{1}{2}eqV_{zz}$  at pyramidal sites (those at tetrahedral sites

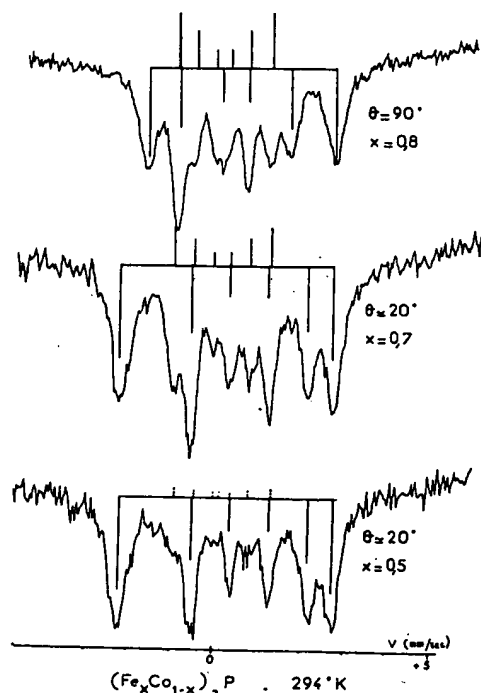
<sup>16</sup> G. K. Wertheim, Phys. Rev. 121, 63 (1961).

TABLE I. Mossbauer parameters at 294°K for  $(\text{Co}_{1-x}\text{Fe}_x)_2\text{P}$ .

$x$	$H_a^1$ (kOe)	$H_a^2$ (kOe)	$\frac{1}{2}eqV_{zz}$	$\eta$	$\theta$
0.8	67	132	0.63	0.46	90°
0.75	69	141	0.67	0.56	90°
0.70	69	153	0.67		20°
0.50	69	153	0.74		20°

assumed negligible), an asymmetry parameter  $\eta$ , and the angle  $\theta$  between the spin direction and the principal axis of the electric-field gradient in the pyramidal sites. The results are summarized in Table I. By symmetry, the principal axis of the electric-field gradient should be perpendicular to the phosphorous canals, so that a  $\theta=90^\circ$  means that the spins are parallel to the  $c$  axis in the hexagonal structure, to the  $b'$  axis in the orthorhombic structure.

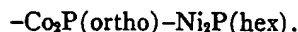
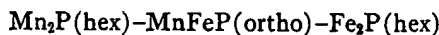
In the range  $x>0.25$ , an increase in the complexity of the spectra (Fig. 17) indicates a spin reorientation. In first approximation and neglecting the asymmetry parameters, a  $\theta\approx 20^\circ$  is obtained with the aid of Kündig's<sup>37</sup> graphs. Since the axes of the pyramidal sites make an angle of about  $30^\circ$  with the orthorhombic  $c'$  axis, it is reasonable to assume that the spins have become oriented parallel to this axis. For  $x=0.25$ , the spins rotate continuously with temperature in the  $b'-c'$

FIG. 17. Rotation of spins as a function of composition in  $(\text{Fe}_x\text{Co}_{1-x})_2\text{P}$ .

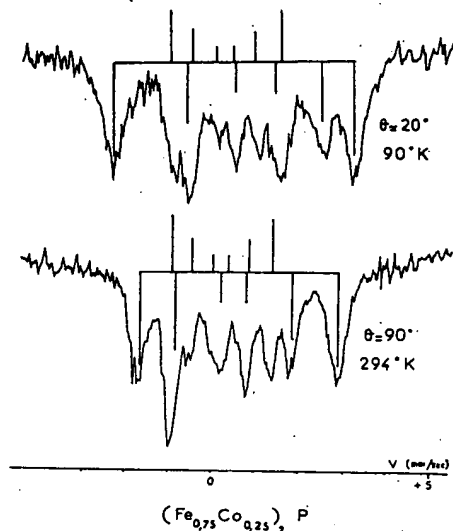
plane: at 90°K they are parallel to  $c'$  and at 294°K to  $b'$  (Fig. 18). These results are confirmed by x-ray diffraction on powder samples oriented in a magnetic field at 294°K. A detailed, complete analysis of the spectra will be published soon.<sup>38</sup>

## VII. DISCUSSION

Mixed phosphides of formula  $M_2\text{P}$  have a remarkable alternation of hexagonal and orthorhombic structures with increasing electron/atom ratio,



Anomalies in the variation with composition of lattice parameters and magnetic properties, which are

FIG. 18. Rotation of spins as a function of temperature in  $(\text{Fe}_{0.75}\text{Co}_{0.25})_2\text{P}$ .

particularly pronounced in the system  $(\text{Co}_{1-x}\text{Mn}_x)_2\text{P}$ , can be attributed, as a result of the Mössbauer studies, to the site preferences of the solute atoms. The completely ordered compounds  $\text{FeMnP}$ ,  $\text{FeCrP}$ ,  $\text{MnCoP}$ , and, without doubt,  $\text{MnNiP}$ , belong to the important family of orthorhombic  $E$  phases represented by  $\text{ZrFeP}$ <sup>39,40</sup>; a homologous family of ordered hexagonal phases would be represented by  $\text{NbMnSi}$ .<sup>41,42</sup> For many members of these families, the ordering energy may be so large that the homogeneity range is strictly limited to the ideal compositions, as in  $\text{ZrFeP}$  and  $\text{NbMnSi}$ .

<sup>37</sup> W. Kündig, Nuclear Instr. Method 48, 219 (1967).

<sup>38</sup> J. P. Senateur, A. Roger, and R. Fruchart (unpublished).

<sup>39</sup> S. Rundqvist and P. C. Nawapong, Acta Chem. Scand. 20, 2251 (1966).

<sup>40</sup> W. Jeitschko, Acta Cryst. 24, 930 (1968).

<sup>41</sup> B. Deyris, J. Roy-Montreuil, R. Fruchart, and A. Michel, Bull. Soc. Chim. de France 4, 1303 (1968).

<sup>42</sup> J. Roy-Montreuil, B. Deyris, R. Fruchart, and A. Michel, Compt. Rend. 264, 587 (1967).

Not only the substitutional ordering, but also deviations from stoichiometry of the metal and not the metalloid atom,<sup>44</sup> suggest that the two structures  $\text{Fe}_2\text{P}$  and  $\text{Co}_2\text{P}$  should both be viewed as metalloid skeletal arrays having twice as many interstitial metal atoms as metalloid atoms and the common, rhombohedral subcell of Fig. 1(b).

Although incomplete, magnetic studies reveal a fundamental difference between the phosphides  $M_2\text{P}$  and  $M_3\text{P}$ : In the systems  $(\text{Fe}_{1-x}M_x)_3\text{P}$ , where  $M = \text{Co}$  or  $\text{Ni}$ , the linear change with  $x$  in magnetization<sup>13,26,27</sup> agrees with the hypothesis of filling of incomplete  $3d$  half-bands, cobalt contributing one and nickel two extra electrons. The magnetization changes by  $0.94 \mu_B/\text{cobalt atom}$  and by  $1.92 \mu_B/\text{nickel atom}$ .<sup>27</sup> Likewise, the abrupt decrease with  $x$  of the magnetization if  $M = \text{Cr}$  shows that the scheme proposed<sup>29</sup> for the borides  $M_2\text{B}$  and  $MB$  applies equally to the  $M_3\text{P}$  phosphides. This scheme uses the virtual-state concept of Friedel,<sup>44,45</sup> which was introduced to account for the magnetic properties of the alloys of the first-row transition metals. Thus the behavior of the compounds  $M_3\text{P}$ , like  $M_2\text{B}$  and  $MB$ , is essentially the same as for the constituent metals, except for the contribution of the metalloid electrons to the  $3d$  bands. Here the metal-atom array forms the skeletal net. On the other hand, the phosphides  $M_2\text{P}$ , although poor in metalloid atoms, exhibit a behavior reminiscent of boron- or phosphorous-rich compounds and compounds having a pronounced

ionic character, such as oxides and sulfides, for which the anionic array provides the structural skeleton. This curious contrast is supported by two additional observations:

1. Although maximum Curie temperatures are high ( $583^\circ\text{K}$ ), nevertheless ferromagnetism is confined to a relatively narrow range of electron/atom ratios in both the  $(\text{Co}_{1-x}\text{Mn}_x)_2\text{P}$  system, which is completely ordered, and the  $(\text{Co}_{1-x}\text{Fe}_x)_2\text{P}$  system, which is partially ordered. (The maximum  $T_c$  would probably occur for  $\text{CoFeP}$  were the atomic ordering complete.)

2. Ferromagnetism is replaced by metamagnetism for electron/atom ratios a little smaller than that of  $\text{CoMnP}$  in the system  $(\text{Co}_{1-x}\text{Mn}_x)_2\text{P}$ . Therefore, it is reasonable to anticipate that  $\text{Fe}_2\text{P}$ , which should have a similar  $3d$  electron/atom ratio, exhibits a magnetization that is extremely sensitive to any reduction in this ratio (whether by substitution of  $\text{Mn}$  or  $\text{Cr}$  or by deviation from stoichiometry,  $\text{Fe}_{2-x}\text{P}$ ) because it is at the critical ratio at which ferromagnetism gives place to metamagnetism. Although not well established by experiment, it appears from the Mössbauer spectra,<sup>38</sup> that small reductions in the electron/atom ratio induce progressively a partial canting of the spins in  $\text{Fe}_2\text{P}$ .

#### ACKNOWLEDGMENTS

This work has been made possible through the aid of the D.R.M.E.

The authors gratefully wish to thank J. B. Goodenough for the help he provided for correcting and presenting the paper at the conference.

<sup>44</sup> S. Rundqvist, Acta Chem. Scand. 14, 1961 (1960).

<sup>45</sup> J. Friedel, Nuevo Cimento Sup. VII 2, 287 (1958).

<sup>46</sup> J. Friedel, J. Phys. Radium 23, 692 (1962).



## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re patent application of

Shigeo T. Oyama

Serial No. 10/089,515

Group Art Unit 1755

Filed July 3, 2002

Examiner Wood, Elizabeth P.

For NOVEL TRANSITION METAL PHOSPHIDE CATALYSTS

Commissioner for Patents  
PO Box 1450  
Alexandria, Virginia 22313-1450

DECLARATION OF SHIGEO T. OYAMA ("TED OYAMA")  
UNDER 37 C.F.R. §1.132

Shigeo T. Oyama declares as follows:

1. I am the inventor of the above-identified application. I am also an expert in the field of catalysts qualified to provide experimental evidence and opinion evidence directed to such matters at the level of skill of one of ordinary skill in the art and obviousness to one of ordinary skill in the art. I have attached hereto a one page, short form resume, to establish my credentials as an expert. As demonstrated by the resume, I hold the degree of Ph.D. in Chemical Engineering; I have been involved in research in Chemical Engineering, Chemistry, and Catalysts for over two decades; I am a titled professor at Virginia Polytechnic Institute & State University; I am a noted author on over 140 refereed publications; I have edited several books; and I am on the Editorial Board of the *Journal of Natural Gas Chemistry*.

2. I have read and understand the application as originally filed, the amendment to be concurrently submitted with this declaration, the office action mailed July 30, 2004, and each of the references cited by the Examiner. It is my opinion that the

claimed invention, particularly as amended in claims 1 and 7, would not be anticipated by or be obvious to one of ordinary skill in the art over U.S. Patents 4,454,246 and 4,359,406 to Fung, the Journal of Catalysis article (XP009009979), or U.S. Patent 4,367,137 to Antos.

#### A. Claimed invention

The claimed invention can best be understood with reference to independent claims 1 and 7, as amended, which recite as follows:

1. (Currently Amended) A catalyst comprising:

a metal phosphide complex having the formula  $MP_x$ , wherein M is selected from the group consisting of V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W, and wherein x ranges from about 0.1 to about 10; and

a high surface area support of at least 50m<sup>2</sup>/g, wherein the metal phosphide complex is dispersed on the high surface area support, wherein said high surface area support is selected from the group consisting of carbon, silica, titania, thoria, magnesia, zirconia, kaolin, bentonite, kieselguhr, zeolites, and combinations thereof.

7. (Currently Amended) A metal phosphide catalyst comprising:

a metal phosphide complex having the formula  $A_aB_bP_y$ , wherein A and B are each selected from the group consisting of V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W, wherein the sum of a and b is 1, the ratio of a and b ranges from about 0.01 to about 100, and y ranges from about 0.1 to about 10; and

a high surface area support of at least 50m<sup>2</sup>/g, wherein the metal phosphide complex is dispersed on the high surface area support, wherein said high surface area support is selected from the group consisting of carbon, silica, titania, thoria, magnesia, zirconia, kaolin, bentonite, kieselguhr, zeolites, and combinations thereof.

It is noted that the claims specify particular metals (V, Cr, Mn, Fe, Co, Ni,

Nb, Mo, Ta, and W) which are "base" metals. In contrast the Fung and Antos patents are directed to "noble" metal phosphides. As will be discussed below in more detail, neither Fung nor Antos describe procedures which would yield metal phosphides from the specified metals (V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W). In view of this, these references do not anticipate and would not make obvious to one of ordinary skill in the art that metal phosphide catalysts of the particular metals (V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W). A person of ordinary skill in the art to which the present invention pertains would typically hold a Ph.D. and typically with 5-15 years research experience after graduation. He or she would have access to a variety of trade journals and reference books in the fields of chemistry, chemical engineering and catalysis, and would be skilled at reviewing the data presented in those references.

Furthermore, the claims specify particular high surface area supports which include carbon, silica, titania, thoria, magnesia, zirconia, kaolin, bentonite, kieselguhr, zeolites, and combinations thereof. Unlike claims 2 and 8 of the application, which have now been canceled, claims 1 and 7, as amended, do not specify alumina as the support. Alumina is the support used in the Nozaki (Journal of Catalysis 79, 207 (1983)) reference identified as (XP009009979). As will be discussed in more detail below, alumina is a poor support for phosphides because of its strong interaction with phosphorous to form aluminum phosphate ( $\text{AlPO}_4$ ) and necessitates the use of higher temperatures for reduction.

#### B. U.S. Patents 4,454,246 and 4,359,406 to Fung

These patents describe the preparation of metal-phosphorous compounds deposited on a high surface area support. While the patents discuss Group VIII metals generally, and Group VIII noble metals specifically, it is noted that the synthesis method described is inappropriate for the non-noble metals. Specifically, the reduction temperature employed in Fung is low (300-500°C), which is appropriate for noble metals, but not for base metals (e.g., V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W).



In Fung, there is described a procedure for impregnation of a support with soluble metal compounds, a phosphorous source, and reduction of the compounds directly in hydrogen, without high temperature calcination. Note particularly Examples 1-2 of the Fung references where there is described low temperature drying at 120°C before reduction. Although, this method works for the preparation of PtP<sub>2</sub> because Pt can be reduced easily. It does not work for non-noble metal phosphides.

In sharp contrast, in the present invention, the metal precursors are first calcined at high temperature to ensure that the components are combined in the form of a phosphate, and then the reducing is performed. If this is not done, the components are not combined, and metal phosphide catalysts will not be produced. To demonstrate this, the following experiments was performed:

#### Method of Reduction of Samples

Phosphide samples supported on a silica support were prepared by impregnating the support with aqueous metal nitrate and ammonium phosphate solutions by the method of incipient wetness impregnation. Prior to use, the silica was dried at 393 K for 3 h and calcined at 773 K for 6 h. The incipient wetness point of the silica was found to be 2.2 cm<sup>3</sup>g<sup>-1</sup>. After impregnation, the powders were dried at 393 K for 3 h and either used as such or calcined at 773 K for 6 h. The reduction of the samples was carried out using temperature-programmed reduction (TPR). The reduction was carried out in a U-shaped quartz reactor placed in a furnace controlled by a temperature programmer (Omega Model CN 2000). A portion of the exit gas flow was sampled through a leak valve into a mass spectrometer (Ametek/Dycor Model MA 100) for following the progress of the reaction. The temperature was monitored by a local chromel-alumel thermocouple placed in a thermowell near the center of the reactor bed. The H<sub>2</sub> flow rate was set at 1000 mol s<sup>-1</sup> (1500 cm<sup>3</sup> min<sup>-1</sup>) per gram sample. The heating rate was 1 K min<sup>-1</sup>.

## Results

### Reduction of Components

Compound	Reduction temperature separate components	Result	Reduction temperature combined components	Result
FeP/SiO <sub>2</sub>	570-700 K (300-430°C)	Metal	930 K (660°C)	phosphide
CoP/SiO <sub>2</sub>	540-590 K (270-320°C)	Metal	830 K (560°C)	phosphide
Ni <sub>2</sub> P/SiO <sub>2</sub>	530-650 K (250-280°C)	Metal	820 K (550°C)	phosphide

As can be seen from the above table, the precursors employed are metal salts like nitrates, and a phosphorous source like ammonium phosphate. The metal has a positive charge which is balanced by the negative nitrate ion and the phosphate has a negative charge which is balanced by the positive ammonium ion. Because the charges are balanced, there is no need for the metal to combined with the phosphate (so the result is a "metal"). However, in the calcination step, the nitrate ion and the ammonium ion are destroyed, to form gaseous nitrogen oxides and ammonia which are released from the solid. This leaves behind the positive metal ion and the negative phosphate species which combine in order to balance their charges.

The table above demonstrates that direct reduction of components, as contemplated by the Fung references, does not work for the base metals recited in the claims. Because the metal component is not combined with phosphorous, the metal is reduced to a metallic state at a low temperature, and then sinters (grows in particle size) as the temperature is raised, precluding its combination with phosphorous.

One of ordinary skill in the art would recognize that the results in the Fung patents are limited to Pt phosphides (this being the only metal where test results

are presented). Further, one of ordinary skill in the art would recognize that Pt is a noble metal, and is chemically different from the base metals recited in the claims. Thus, one of ordinary skill in the art would recognize that Fung's data could not be extended to all group VIII metals. This is verified by the results in the Table above.

C. U.S. Patent 4,367,137 to Antos et al.

This patent describes an acidic catalytic composite composed of a carrier metal supporting a platinum group metal, cobalt, tin, phosphorous, and halogen. It is noted that nowhere in Antos is it demonstrated that a phosphide is formed. Rather, only a brief statement in the text alludes to this, but acknowledges uncertainty. See particularly column 14 where it is stated:

"Despite the fact the precise form of the chemistry of association of the phosphorous component with the catalytic composite of the present invention is not known, it is believed to be most intimately related with the cobalt component of the catalytic composite, although it may be associated physically and/or chemically with the carrier material and/or the platinum group and tin components"... "it is believed that best results are obtained when the phosphorous component exists in the catalytic composite substantially in the form of a phosphide with the cobalt component."

In fact, the procedures used by Antos would not yield a metal phosphide as claimed by the present application. This is because the temperature used in Example II of Antos (reduction of the Co and P containing composite at 975 °F (524°C), is too low for phosphide formation. As evidence of this, attached hereto are the following:

- 1) Goodenough, *J. Appl. Phys.* Vol. 40, p. 1250 (1969). This document reports that phosphide formation takes place between 850-900°C between metal and phosphorous. See also, Schonbert, *Acta Chemica Scandinavica* 8:226-239 (1954)
- 2) Wang et al. *J. Catalysis* 208-321-331 (2002). This document, on which I am noted as joint-author, shows that with Co/P, major reduction took place at 820 K

(550°C), but completion required 690°C. (See Figure 4 on page 325). This corresponds to Example 5 of the present application where 690°C was used.

Based on these reported results, as well as the lack of data and analysis in Antos, and Antos' own statements of uncertainty, it should be concluded that Antos does not suggest a methodology which would yield metal phosphide catalysts which fall within the ambit of the claims of the present application. Thus, one of ordinary skill in the art would not find Antos as suggesting the claimed invention.

D. Nozaki et al, *Journal of Catalysis* 79, 207 (1983)

In this paper, the authors report catalysts composed of  $\text{Ni}_2\text{P}$ ,  $\text{Co}_2\text{P}$ , and  $\text{FeP}$  deposited on an alumina support. The catalysts were obtained from phosphate precursors by reduction in hydrogen.

One of ordinary skill in the art will recognize that the use of other supports, as set forth in independent claims 1 and 7, provide certain new and unobvious advantages over alumina supports. In fact, alumina is a poor support for phosphides, as it interacts very strongly with the phosphorus forming an aluminum phosphate ( $\text{AlPO}_4$ ) and necessitates that use of high temperatures of reduction. The attached figures, which are taken from referenced publications on which I am noted as a joint author, show reduction provides for the different catalysts obtained by following the production of water as a function of temperature. In all cases, the precursor is a phosphate which undergoes reduction to a phosphide.

Attached Figure 1 shows the reduction profile of pure MoP and  $\text{MoP/SiO}_2$  (see, Clark et al., *J. Catal.* 207,256, (2002) attached). Figure 2 shows the reduction provide for  $\text{MoP/Al}_2\text{O}_3$  (see, Clark et al., *J. Catal.* 218, 78 (2003) attached). As can be seen, the reduction for  $\text{MoP/SiO}_2$  requires only 820 K (547°C), while that for  $\text{MoP/Al}_2\text{O}_3$  necessitates 1170 k (900°C). Published work also shows that this is because of the formation of the  $\text{AlPO}_4$  phase as a result of the strong interaction between Al and P.

Similar results are found for  $\text{Ni}_2\text{P}$  on other supports claimed in the present

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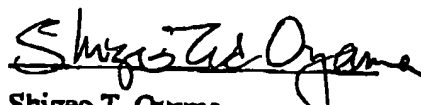
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application. Attached Figure 3 compares the synthesis of  $\text{Ni}_2\text{P}$  supported on two zeolites (KUSY, potassium promoted ultra-stable Y) and MCM-41, to  $\text{Ni}_2\text{P}$  supported on silica and  $\text{Ni}_2\text{P}$  supported on  $\text{Al}_2\text{O}_3$ . The reduction temperatures for the KUSY, MCM-41, and  $\text{SiO}_2$  supports are between 860-880 K (590-610° C), whereas that for  $\text{Al}_2\text{O}_3$  support is at 1270 K (1000°C). The presence of  $\text{Ni}_2\text{P}$  has been confirmed on all these supports by x-ray diffraction and x-ray absorption measurements. This work shows that supports other than alumina can produce the phosphide at much lower temperatures. This is a non-obvious, and highly important finding.

Attached Figure 4 shows the results of preparing MoP, WP, and  $\text{Ni}_2\text{P}$  using a carbon support. Again, the reduction temperatures are low, ranging from 810-860 K (540-590°C).

3. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. 1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Date: Nov 16, 2004

  
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Chairman, Gordon Conference on Hydrocarbon Resources, 1994  
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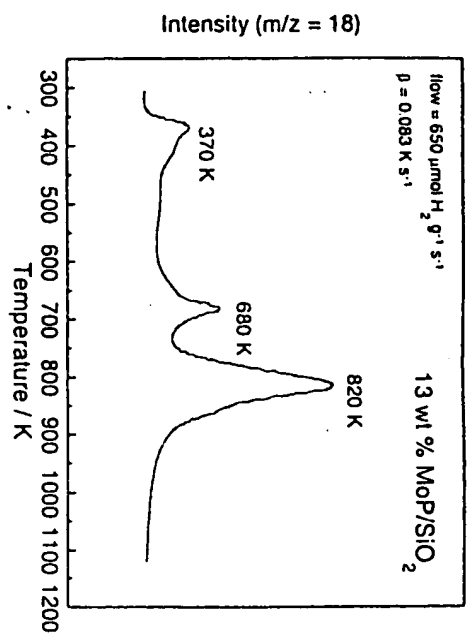


Figure 1 Synthesis of MoP/SiO<sub>2</sub>

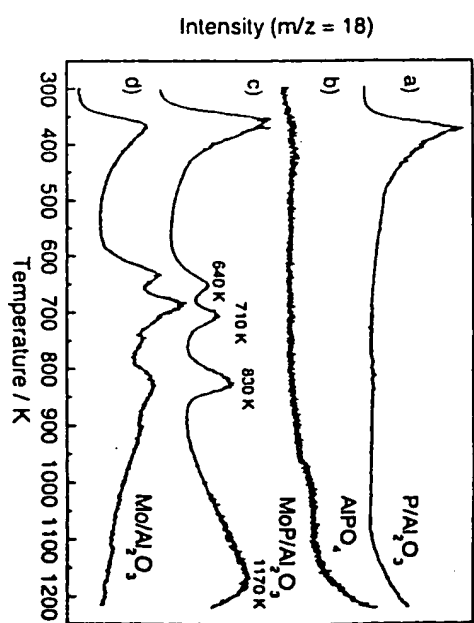


Figure 2. Synthesis of MoP/Al<sub>2</sub>O<sub>3</sub>

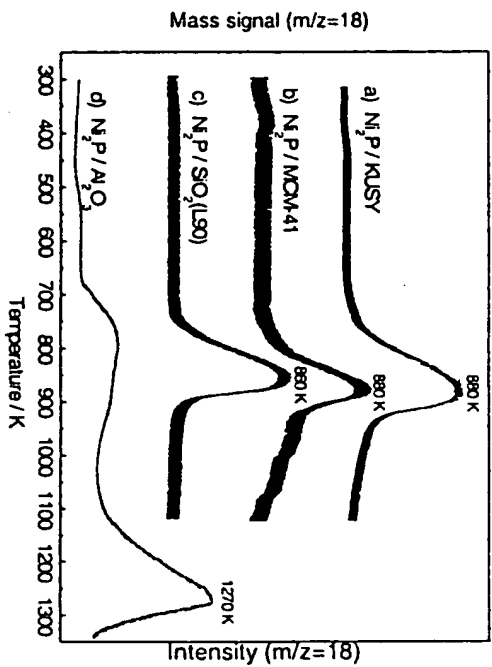


Figure 3. Synthesis of Ni<sub>2</sub>P on various supports

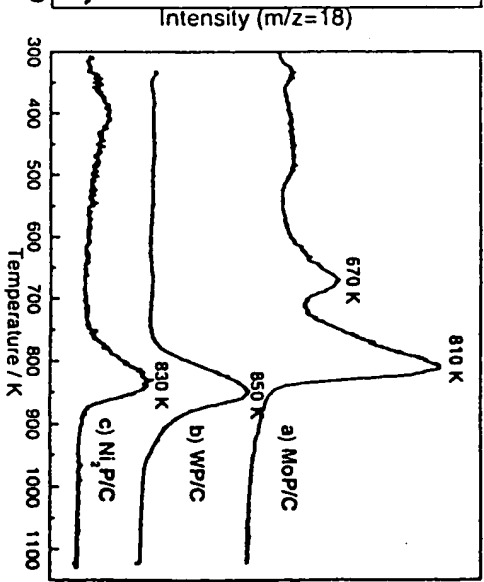
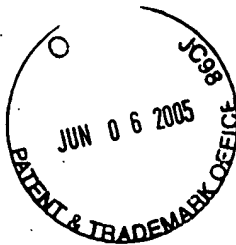


Figure 4. Synthesis of phosphides on carbon



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Docket No. 10/89,515 In re: ✓ patent/     trademark application of

Applicant(s) Eyama

Serial No. 10/89,515 Date Filed 7-3-02

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